SELECTIVE BIOSORPTION OF SILVER IONS FROM AQUEOUS SOLUTION USING CHITOSAN-BASED BIOSORBENTS

by

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ABSTRACT

In this study, Ag^{+}-imprinted thiourea/glutaraldehyde grafted O-carboxymethyl chitosan (ITG-OCMC) beads and Ag^{+}-imprinted glutaraldehyde-crosslinked chitosan (IGCC) gel beads were synthesized to selectively adsorb Ag^{+} from bimetallic aqueous solutions containing the same molar concentration of Ag^{+} and Cu^{2+}. Surface imprinting technology has been applied to achieve extremely high selectivity for Ag^{+} on the prepared sorbents by generating recognizable binding sites. For the ITG-OCMC beads, experimental results indicated that high degree of carboxymethylation and low level of crosslinking would help to achieve higher uptake capacity of Ag^{+}. The maximum uptake of Ag^{+} was found to be 156.32 mg g^{-1} at 40.0 °C with an initial Ag^{+} concentration of 160.50 mg L^{-1} and the biosorbent dosage of 1.0000 g L^{-1}. Langmuir isotherm and Lagergren's pseudo-second-order kinetics can be used to describe the sorption process of Ag^{+}. Analyses from FTIR and XPS confirmed that selective adsorption of Ag^{+} took place on the surfaces of ITG-OCMC beads by chelation through >C=S, amine, carboxyl and hydroxyl groups. For the IGCC beads, the maximum uptake of Ag^{+} by the ion-imprinted chitosan beads was found to be 89.200 mg g^{-1} at 25.0 °C with an initial Ag^{+} concentration of 352.95 mg L^{-1} and the biosorbent dosage of 1.0000 g L^{-1}. The adsorption equilibrium and kinetics of Ag^{+} by IGCC beads can be better described by Langmuir isotherm and the intraparticle diffusion model. FTIR and XPS analyses suggested that amine functional groups involve the binding of Ag^{+} via complexation at higher solution pH ($3.0 \leq pH \leq 5.0$) and ion exchange at lower solution pH ($1.0 \leq pH < 3.0$).

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List of Abbreviations

BE	Binding energy
CMC	Carboxymethyl chitosan
DOE	Design of experiment
ECH	Epichlorohydrin
EDGE	Ethylene glycol diglycidyl ether
EDTA	Ethylene-diaminetetraacetic acid
FTIR	The Fourier transform infrared
HSAB	Hard and soft acids and bases
ICP-OES	Inductively coupled plasma optical emission spectrometer
IGCC	Ag^{+}-imprinted glutaraldehyde-crosslinked chitosan
IIP	Ion-imprinted polymers
ITG-OCMC	Ag^{+}-imprinted thiourea/glutaraldehyde grafted O-carboxymethyl chitosan
MIP	Molecularly imprinted polymers
OCMC	O-carboxymethyl chitosan
TG-OCMC	Thiourea/glutaraldehyde grafted O-carboxymethyl chitosan
XPS	X-ray photoelectron spectra

Chapter 1 Introduction and Overview

1.1. INTRODUCTION

Chitosan, which is the N-deacetylated derivative of chitin, has drawn much commercial attention. Different from synthetic polymers, chitosan, as a natural polymer, presents excellent biodegradability and biocompatibility (Kumar, 2000). Together with its nontoxicity, chitosan has been intensively utilized in biomedical field, for example, drug delivery (Agnihotri et al., 2004; Bhattarai et al., 2010; Nagpal et al., 2010; Park et al., 2010; Riva et al., 2011), tissue engineering (Madihally and Matthew, 1999; Suh and Matthew, 2000; Di Martino et al., 2005; Kim et al., 2008), ophthalmology (Felt et al., 1999; Kumar, 2000; Peptu et al., 2010), wound dressing (Kumar et al., 2004; Yudanova and Reshetov, 2006; Muzzarelli et al., 2007; Xie et al., 2008; Pillai et al., 2009). Chitosan, compared to other natural polymers, presents a large capacity for chelating transition metals due to its free amino functional groups (Muzzarelli, 1973). The chelating property of chitosan makes it a good candidate as a biosorbent for recovering metal ions from industrial metal-bearing effluents (Veglio and beolchini, 1997; Guibal et al., 1998; Wu et al., 2001; Babel and Kumiawan, 2003; Gerente et al., 2007).

Chitosan in its original form is not suitable for practical use as a metal sorbent because it is soluble in dilute aqueous acids and many industrial metal-bearing wastewater and effluents tend to be acidic. Chemical modifications of chitosan are

therefore essential to improve its chemical stability, mechanical strength and adsorption capacity under acidic environment. In general, chitosan can be modified by utilizing the reactivity of the primary amino group and the primary and secondary hydroxyl groups through crosslinking, grafting of new functional groups, and acetylation (Wang and Chen, 2014). The crosslinking of chitosan usually utilizes bi/polyfunctional crosslinking agents such as glutaraldehyde, ethylene glycol diglycidyl ether, tripolyphosphate, and epichlorohydrin (Sureshkumar et al., 2010). Although the chemical stability and mechanical strength of chitosan can be enhanced remarkably, the metal uptake capacity of chitosan sorbent is significantly decreased after crosslinking. Grafting new functional groups (such as amino, carboxylic, phosphate groups, and sulfur-containing compounds) onto chitosan, and hence increasing the density of sorption site, is widely explored to increase the sorption capacity of metal ions (Varma et al., 2004; Jayakumar et al., 2005). Recently, ion-imprinted chitosan with target metal as template has also been developed to increase the selectivity of the sorbent to work in wastewater containing multi-metal ions (Sun et al., 2006).

So far, chitosan based biosorbents have been extensively applied to remove toxic heavy metals, such as lead (Jin and Bai, 2002; Yan and Bai, 2005), mercury (Jeon and Park, 2005; Li et al., 2005), copper (Chu, 2002; Ngah et al., 2004; Li and Bai, 2005), or to recover precious metals, for example, gold (Wan Ngah and Liang, 1999; Arrascue et al., 2003; Fujiwara et al., 2007; Ramesh et al., 2008), platinum (Guibal et al., 1999;

Fujiwara et al., 2007; Ramesh et al., 2008), and palladium (Chassary et al., 2005) from wastewater.

Silver is a noble metal that has been widely employed in the photographic and electrical industries for many years. It is known to be released to the environment through its industrial applications, leading to possible exposure to aquatic organisms (Pedroso, et al., 2007). The removal or recovery of silver ions using chitosan based sorbents has not been thoroughly investigated. Therefore, the recovery of silver from industrial wastewater and effluents using low-cost and high-capacity chitosan based biosorbents has great scientific value (Wen et al., 2002; Mack et al., 2007).

As a result, selective biosorption of silver ions from aqueous solution using chitosan-based biosorbents was selected as the topic of current study.

1.2. LITERATURE REVIEW

1.2.1. Biosorption

As defined by G. M. Gadd, biosorption is a physicochemical and metabolically independent process which can remove organic and inorganic substances from solutions by biological material with different mechanisms, namely absorption, adsorption, ion exchange, surface complexation and precipitation (Gadd, 2009). Biosorption research, which was originally focused on metal uptake from aqueous solutions, has expanded to particulates and colloids as well as inorganic and organic compounds including dyes, fluoride, phthalates, and pharmaceuticals (Chiou and Li,

2003; Chen et al., 2007; Ma et al., 2007; Fomina and Gadd, 2014). However, most of the research still concentrates on the removal of metal ions. Several conventional technologies have been applied to metal recovery, including chemical precipitation (Kunda, 1983; Ivanova et al., 1999), ion exchange (Cooley, 1981; Atluri and Raghavan, 1988), cementation (Gerhartz, 2003; Aktas, 2008), evaporation (Volesky, 2001), electrowinning (Chatelut et al., 2000; Juarez and Dutra, 2000; Gerhartz, 2003), and reverse osmosis (Jeppesen et al., 2009; Koseoglu and Kitis, 2009). As listed in Table 1.1, each technology mentioned above has its disadvantages that limit its applications. In summary, their applications have been limited due to high capital cost, incomplete recovery or high consumption of reagents and energy. Compared with these traditional approaches for metal recovery, biosorption is regarded as a cost-effective and eco-friendly technology, especially for trace amounts of metal in solutions (Sud et al., 2008; Farooq, 2010). Although great efforts have been made to prepare biosorbents for wastewater treatment, there has been little or no successful application on an industrial scale. According to Fomina and Gadd (2014), the main reasons for the unsuccessful commercial application are the low technology readiness level, such as poor understanding of the mechanisms, kinetics and thermodynamics of the process, and the questionable stability and predictability of the biosorption process, especially when compared with ion exchange resins, which provide fidelity and predictability. As a result, biosorbent preparation is crucial for exploring the fundamentals and commercialization of biosorption technology.

Table 1.1 Advantages and disadvantages of traditional metal recovery methods

Method	**Advantages**	**Disadvantages**
Chemical Precipitation	Simple	For high concentration only
	Cheap	Separation required
		Generates sludge
Ion Exchange	Effective	Sensitive to particles
	Easy recovery	Expensive
Cementation	Cheap	Relatively low efficiency
		Refinery of targeted metal is expensive
Electrowinning	Effective at high concentration only	Second treatment is required
		Incomplete removal
Evaporation	Pure effluent	Expensive
		Generates sludge
Reverse Osmosis	Pure effluent	Expensive
		High pressure required

1.2.1.1. Evaluation of biosorbents

There are several widely used criteria for sorbent screening: capacity, selectivity, regenerability, mass transfer kinetics, and cost (Knaebel, n.d.). It is unlikely that a biosorbent can satisfy all these aspects, so certain attributes will be given more weight when evaluating a particular kind of biosorbent.

Capacity (q_e) is the amount of metal ions sequestered per unit mass of sorbents, which can be defined as follows:

$$q_e = \frac{C_i - C_e}{m} \times v \qquad \text{Eq. (1-1)}$$

where C_i and C_e are the initial and equilibrium concentrations of metal ions, v is the volume and m is the dry weight of the biosorbent. Capacity is an important criterion for screening biosorbents, which characterizes the performance at a high residual concentration. The capacity, also known as the maximum sorption uptake value, depends on the initial concentration of the solution, temperature of the environment and the amount of biosorbent used.

Selectivity is another important criterion for evaluating the performance of biosorbents, especially for multi-metallic biosorption, which is a common phenomenon in wastewater and industrial effluents. The simplest definition of selectivity is the ratio of the capacity of one component to that of another at a given concentration; in other words, a biosorbent with high selectivity will uptake as much of the interested component while uptake as little of any other component. As almost all kinds of wastewater and industrial effluents contain more than one component, the selectivity is even more important than the capacity. However, most of the research in the area of biosorption focuses on the sorption of a monometallic system, pursuing higher capacity without competitive sorption. But the presence of co-existing metal ions will affect the selectively uptake of the targeted metal ions. Usually, the co-existing metal ions compete with the targeted metal ions for binding sites and thus lower the uptake of the

biosorbent (Mack et al., 2007). Therefore, the investigation of the selective biosorption of a specific metal ion from multi-metallic environments is more important and valuable. Simultaneously, the involvement of co-existing metal ions in addition to the targeted metal ion will dramatically increase the difficulty in explaining the mechanism, kinetics and thermodynamics of the process. Investigation using a binary system is a compromising solution, which obtains all uptake data under competitive sorption while keeping the interpretation of the mechanism, kinetics and thermodynamics of the process practicable.

Regenerability is an ignored aspect that has not been addressed in many publications. However, industrial applications need the biosorbent to operate in sequential cycles with uniform performance. As a result, regenerability is as important as selectivity, especially for biosorbents prepared for industrial applications. Regenerability is the comprehensive evaluation of the retained fraction of the original capacity and the time and energy required for the regeneration. Cyclic biosorption application needs the bindings between adsorbents and adsorbates to be relatively weak. In other words, the heat of adsorption, which provides a measure of required energy for regeneration, should be low. The capacity of biosorbents will show a gradual decay after sequential cycles, due to the aging and poisoning of the biosorbent.

Mass transfer kinetics is important because it dominates the cycle time of the biosorption process. Ideally, biosorbents should uptake the targeted component as fast as possible, which means that the cycle time must be short, to make the biosorbent

efficient.

Cost, obviously, is another important aspect. Cost-effective biosorbents demand cheap and easily acquired raw materials, simple modification, low operation cost, better regenerability, and fewer reagents and energy consumption during the whole process.

1.2.1.2. Raw material of biosorbents

Major source categories for biosorbents have been summarized as follows (Park et al., 2010):

- Bacteria: gram-positive and gram-negative bacteria, cyanobacteria
- Fungi: molds, mushrooms and yeasts
- Algae: micro-algae, macro-algae such as, brown and red seaweeds
- Industrial waste: activated and anaerobic sludge, waste from fermentation, food or beverage industries
- Agricultural waste: Fruit or vegetable wastes, rice straws, soybean hulls
- Biomass residues: plant residues, sawdust, tree bark, weeds
- Other biomaterial: chitin, chitosan, cellulose, alginate

Among the large biomass resource pools, chitosan (from chitin) has been chosen to be the starting material in this study, because it has proved to be an efficient metal scavenger due to the presence of reactive amino and hydroxyl groups. Moreover, chitosan is a wise choice as the starting material for biosorbent preparation for a coastal

province like Newfoundland and Labrador, as it can be acquired from shellfish waste from the food processing industry.

1.2.1.3. Modification of biosorbents

In order to increase the specific surface area and accelerate the mass transfer, powders are the most widely used form of biosorbents, but from the industrial application point of view, powder form is not suitable to be packed in a column because it may cause clogging problems, huge pressure drops, or serious hydrodynamic limitations (Wang and Chen, 2014). Among the various forms of biosorbents, namely powder, beads, resin, etc., gel beads are considered the best form of sorbents for recovering metal ions from aqueous solutions (Guibal, 2004). Therefore, immobilization is necessary for practical implementations.

The ideal commercial biosorbents will also need to have high capacity, selectivity, and stability, which means modifications are necessary. A number of physical and chemical technologies have been applied for the modifications of biosorbents. Physical modification methods, including autoclaving, steam, thermal drying, lyophilization, cutting, grinding, and so on, are considered as simple, inexpensive, but less effective approaches (Park et al., 2010). Among the chemical modification technologies, several technologies have been proven to be effective, such as crosslinking, imprinting, and grafting of certain functional groups.

In order to increase the chemical stability and mechanical strength of sorbent beads, crosslinking is necessary, because crosslinking can form chemical bonding

between carbon chains. However, certain functional groups on the carbon chains of chitosan, which serve as effective adsorption sites for target metals, will inevitably be involved in this process. As a result, crosslinking may decrease the capacity of prepared sorbents, as some of the adsorption sites are occupied (Wan Ngah and Fatinathan, 2010). Different kinds of crosslinking agents have been successfully used for crosslinking chitosan, such as formaldehyde, glutaraldehyde, ethylene glycol diglycidyl ether (EDGE), and epichlorohydrin (ECH) ethylene-diaminetetraacetic acid (EDTA) (Wan Ngah et al., 2002; Repo et al., 2010; Wan Ngah and Fatinathan, 2010; Monier, 2012). Among these crosslinking agents, glutaraldehyde and formaldehyde are the simplest to crosslink and are the most widely used, easy to get, and relatively cheap reagents. As a result, glutaraldehyde and formaldehyde have been chosen to be the crosslinking agents for comparison in this study. Possible reaction schemes of formaldehyde crosslinked chitosan and glutaraldehyde crosslinked chitosan can be found in Figure 1.1 and Figure 1.2, respectively.

Surface imprinting technology has drawn much attention to generate recognition sites, and has been successfully used to prepare metal ion imprinted materials through the use of various templates (Fan et al., 2011; Branger et al., 2013). The coordination between the imprinted ions and the monomers can be based on non-covalent interactions, such as hydrogen bonds, electrostatic interactions, hydrophobic effects, Van der Waals forces, etcetera, or reversible covalent bonds (Rao et al., 2006). The successful applications of imprinting technology to prepare biosorbents for metal ions

biosorption are shown in Table 1.2.

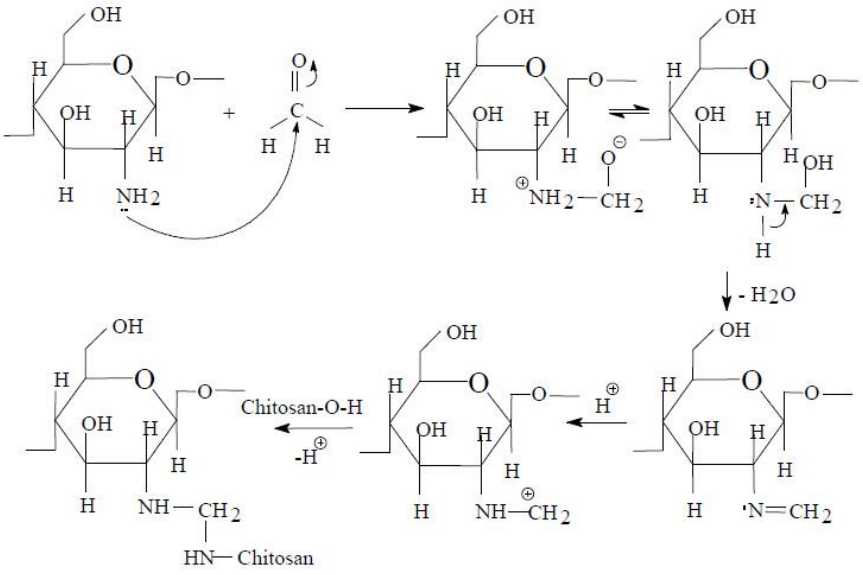

Figure 1.1. Possible reaction of the crosslinking of chitosan with formaldehyde.

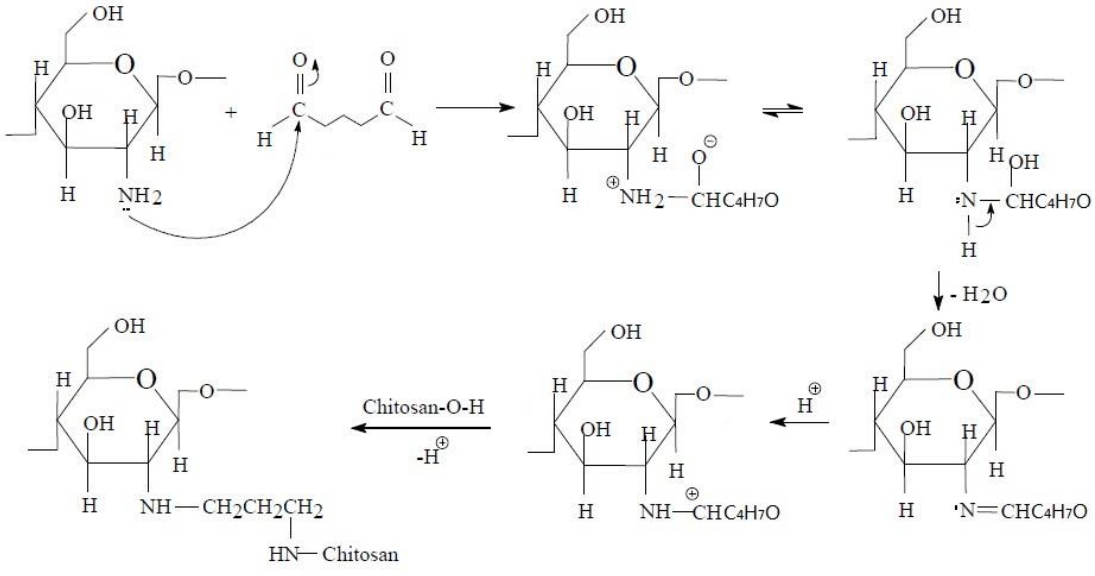

Figure 1.2. Possible reaction of the crosslinking of chitosan with glutaraldehyde.

Table 1.2 Applications of imprinting technology to enhance sorption capacity for a variety of adsorbents

Element	Biosorbent	Capacity w/o imprinting mg g^{-1}	Reference
Ag	Magnetic thiourea-chitosan	496.8 /265.68	Fan et al., 2011
Ag	Chitosan based solid particles	9.6 /1.97	Hou et al., 2015
Ag	Chitosan based hollow particles	14.2/2.1	Hou et al., 2015
Ag	Chitosan based single hole hollow particles	19.8 /7.9	Hou et al., 2015
Ag	Chitosan based Janus hollow particles	13.6 /3.2	Hou et al., 2015
Ag	Chitosan hydrogel	11.43 /8.66	Song et al., 2012
As	Chitosan resin	2.16 /1.62	Liu et al., 2012
Cd	Chitosan resin	132.63 /86.55	Liu et al., 2011
Cu	Chitosan Schiff's base	20.96 /12.19	Chen et al., 2011
Cu	N-succinyl-chitosan	133.98/117.48	Sun et al., 2007
Hg	Chitosan thioglyceraldehyde Schiff's base	137.13 /77.51	Monier & Abdel-Latif, 2013
Ni	Chitosan microparticles	29.94 /19.07	Chen et al., 2011

Ni	Chitosan coated mycelium	86.5 /56.2	Su et al., 2006
Ni	Chitosan resin	50.9 /25.9	Tan et al., 2001
Pb	Chitosan microparticles	74.59 /51.8	Chen et al., 2011
Pb	Carboxymethyl chitosan	430.98 /31.08	Sun et al., 2006
Zn	Chitosan microparticles	14.41 /9.82	Chen et al., 2011
Zn	Carboxymethyl chitosan	133.62 /27.51	Sun & Wang, 2006

1.2.2. Applications of chitosan based biosorbents

As described by M. Rinaudo (2006), when the degree of deacetylation of chitin reaches 50%, chitin turns into chitosan which is soluble in aqueous acidic solutions. Degree of acetylation of chitosan and molecular weight are two important characteristics for chitosan. As shown in Figure 1.1, chitosan contains free amino and hydroxyl groups. The -NH_2 groups at the C-2 position and the –OH groups at the C-3 and C-6 positions are reported to be involved in modification reactions and the chelation of metal ions. Not only the amount of these functional groups, but also the distribution of them will affect the chelation of metal ions (Kurita et al., 1979).

As the only pseudonatural cationic polymer, the possibility of using chitosan as the starting material for biosorbent preparation has been extensively investigated. Chitosan based biosorbents have been widely used for the removal/recovery of heavy metals and precious metals.

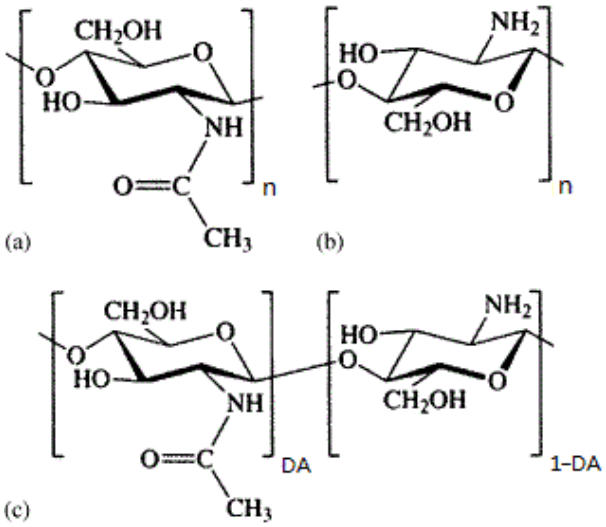

Figure 1.3. Chemical structure of chitin (a) and chitosan (b) repeat units, and the structure of partially acetylated chitosan (c).

Note: DA is the average degree of acetylation.

1.2.2.1 Biosorption of metal ions using chitosan based biosorbents

Table 1.3 summarizes the research results of the biosorption of metal ions other than Ag^{+} and Cu^{2+} using chitosan based biosorbents. The results indicate that grafting is an effective approach to minimize the capacity degradation of biosorbents due to crosslinking (Donia et al., 2008). Certain functional groups, which are favourable to selectively adsorb target metals, can be introduced to the carbon chain to increase both the capacity and selectivity. Carboxymethylation has been proved to be efficient to enhance the capacity and selectivity of precious metal (Hon and Tang, 2000; Chen and Park, 2003; Choong and Wolfgang, 2003).

Table 1.3 Application of biosorption of metal ions using chitosan based biosorbents

Element	Capacity mg g^{-1}	Modification	Reference
As(V)	1.37	-	Gerente et al., 2010
As(III)	70	Molybdate impregnated	Dambies et al., 2002
As(V)	230	Molybdate impregnated	Dambies et al., 2002
As(V)	97.37	Glutaraldehyde crosslinked Molybdate oxoanions	Elwakeel, 2014
As(III)	94	Zerovalent iron	Gupta et al., 2012
As(V)	119	Zerovalent iron	Gupta et al., 2012
Au	453.1	Sodium tripolyphosphate crooslinked	Donia et al., 2013
Au	33.9	N-carboxymethylation	Wan Ngah & Liang, 1999
Au	1639.04	Carboxymethylation Grafting sulfur groups Glutaraldehyde crosslinked	Wang et al., 2012
Cd	85.47	-	Sankararamakrishnan et al., 2007
Cd	357.14	Grafting xanthate group	Sankararamakrishnan et al., 2007
Cd	168.6	Glutaraldehyde crosslinked	Dzul Erosa et al., 2001
Hg	181.8	EGDE crosslinked	Li et al., 2005

Hg	322.6	Polyacrylamide grafted EGDE crosslinked	Li et al., 2005
Hg	539.59	Ethylenediamine aminated Epichlorohydrine crosslinked	Zhou et al., 2010
Hg	461.36	Ethylenediamine aminated Glutaraldehyde crosslinked	Jeon & Holl, 2003
Pb	34.98	NaOH immobilized	Wan Ngah & Fatinathan, 2010
Pb	370.63	Triethylene-tetramine grafted	Kuang et al., 2013
Pb	79.2	Microfludic, Pb(II) imprinted Glutaraldehyde crosslinked	Lu et al., 2013
Pt	171	Ethylenediamine aminated Glutaraldehyde crosslinked	Zhou et al., 2010
Pt	129.9	Thiourea grafted Epichlorohydrin crosslinked	Zhou et al., 2009
Pd	138	Ethylenediamine aminated Glutaraldehyde crosslinked	Zhou et al., 2010
Pd	112.4	Thiourea grafted Epichlorohydrin crosslinked	Zhou et al., 2009

1.2.2.2 Biosorption of Cu^{2+} using chitosan based biosorbents

As the binary solution containing the same mole concentration of Ag^{+} and Cu^{2+} is

chosen to perform all sorption tests, the mechanisms of Cu^{2+} biosorption onto chitosan based biosorbents are crucial.

Poly(vinyl alcohol) blended chitosan beads were prepared by Wan Ngah et al. (2004), and the highest uptake of Cu^{2+} was found to be 47.85 mg g^{-1}. Hydroxyl and amine groups are reported to be the functional groups which were involved during the adsorption.

Chitosan-cellulose hydrogel beads were successfully developed by Li and Bai. (2005). The highest uptake of Cu^{2+} was 53.2 mg mL^{-1} of wet resin at neutral pH. FTIR and XPS results indicated that N atoms in chitosan were the main binding sites for Cu^{2+} to form surface complexes.

Wang et al. (2014) prepared Cu^{2+}-imprinted chitosan hydrogel was prepared by UV-initiated simultaneous free radical/cationic hybrid polymerization. The highest uptake of Cu^{2+} was found to be 40.64 mg g^{-1}. The Cu^{2+} adsorption was mainly interacted with the amide and ether groups.

Glutaraldehyde and epichlorohydrin crosslinked chitosan were obtained by Vieira et al. (2011). XPS results indicated that glutaraldehyde crosslinking occurred preferentially on amino groups while epichlorohydrin crosslinking favourably took place on hydroxyl groups. Metallic copper was only found after adsorption on glutaraldehyde-crosslinked chitosan.

Ethylenediamine modified ethylene glycol diglycidyl ether crosslinked chitosan resin was prepared by Elwakeel et al. (2013). The highest uptake of Ag^{+} was found to

be 146.88 mg g^{-1} at 25 ℃ . However, the selectivity of the prepared sorbent was not reported.

In summary, the adsorption of Cu^{2+} onto chitosan based biosorbents mainly occurred on N and O atoms of chitosan. Therefore, the adsorption of Ag^{+} and Cu^{2+} onto chitosan based biosorbents is competitive. As a result, sulfur group grafting and Ag^{+}-imprinting were essential to increase the selectivity of chitosan based biosorbents towards Ag^{+}.

1.2.3. Silver Recovery

Regarding toxicity, heavy metals, for example copper, lead and mercury, are considered more toxic to the environment. On the other hand, from the economic value perspective, silver is not as expensive as other precious metals, such as gold and platinum. As a result, more research interests have been leaned towards the recovery or treatment of metals such as lead, mercury, gold, and platinum, and the number of publications about silver is relatively low. Silver has been widely used in mircroelectronic devices (Hsu and Wu, 2007; Park et al., 2008), antibacterial materials (Morones et al., 2005; Martinez-Castanon et al., 2008), catalytic materials (Shiraishi and Toshima, 1999), sensor materials (Mcfarland and Van Duyne, 2003), and especially photographic materials, due to its superior malleability, ductility, electrical conductivity, antimicrobial activity, thermal conductivity and photosensitivity (Sneha et al., 2010). As a result, significant amounts of silver have been discharged in the wastewater from such industries. In addition, mining effluents also contain appreciable amounts of silver,

since silver is usually distributed with relatively low content in massive base metal ores. As a matter of fact, since 2005, world silver demand, which steadily increases by around 2-2.5% annually, has exceeded production (Butterman and Hilliard, 2005; GMSF, 2011). About 18-20% of the world's silver demand is supplied by recycling photographic wastes. From the toxicity point of view, silver ions in wastewater are not as harmless as people usually thought. Actually, silver ions are more toxic for fish than copper or mercury (Ratte, 1999; Wood et al., 1999; Lee et al., 2005; Hiriart-Baer et al., 2006), and the accumulation of silver ions in organisms (including humans) can cause numerous diseases and disorders (Rosenman et al., 1979; US Environmental Protection Agency, 1985; Rosenman et al., 1987). In summary, it is essential to efficiently and economically recover silver from industrial wastewater and effluents.

1.2.3.1. Biosorption of silver

Table 1.4 summarizes the research results of the biosorption of silver using biosorbents other than chitosan based sorbents. The uptake of Ag^{+} varies greatly, and the highest capacity among the listed biosorbents is 420 mg g^{-1} of Sargassum natans.

Table 1.4 Application of silver biosorption of various bioadsorbents

Biosorbent	**Capacity mg/g**	**Reference**
Aspergillus niger	98.75	Akthar et al., 1995
Neurospora crassa	68.25	Akthar et al., 1995
Fusarium oxysporium	57.50	Akthar et al., 1995

Saccharomyces cerevisiae	60.05	Simmons and Singleton, 1996
Chlorella vulgaris	56.7	Cordery et al., 1994
Calcium alginate	52	Torres et al., 2005
Bacillus cereus	91.75	Li et al., 2010
Myxococcus xanthus	47.52	Merroun et al., 2010
Streptomyces rimosus	63	Bakhti and Selatnia, 2008
Tremella sp. UFMG-Y07	38.2	Gomes et al., 1999
Candida guilliermondii UFMG-Y22	36.6	Gomes et al., 1999
Candida Guilliermondii UFMG-Y23	46.0	Gomes et al., 1999
Rhodotorula mucilaginosa UFMG-Y27	19.3	Gomes et al., 1999
Aureobasidium pullulans UFMG-Y28	18.3	Gomes et al., 1999
Geotrichum sp. UFMG-Y33	35.7	Gomes et al., 1999
Paecilomyces lilacinus	101.0	Ou et al., 2011
Valonia tannin	97.08	Yurtsever and Sengil, 2012
C. cladosporioides Strain 1	0.6	Pethkar et al., 2001
C. cladosporioides Strain 2	0.12	Pethkar et al., 2001
Strains BP 7/26	144	Tsezos et al., 1995
Strains BP 7/15	131	Tsezos et al., 1995
Strains CH 34	86	Tsezos et al., 1995
Strains ER 121	117	Tsezos et al., 1995
Strains AS 302	115	Tsezos et al., 1995

Strains MB 127	115	Tsezos et al., 1995
Rhizopus arrhizus	54	Tobin et al., 1984
Saccharomyfces cerevisae	40	Volesky, 1990
Bacillus subtilis	90	Volesky, 1990
Sargassum natans	420	Volesky, 1990
Chondrus crispus	98	Volesky, 1990
Chlorella vulgaris	115	Volesky, 1990

1.2.3.2. Biosorption of silver ions from monometallic solutions using chitosan based biosorbents

Although chitosan has proved to be a promising raw material for biosorbent preparation, only few publications have been dedicated to the biosorption of silver using chitosan based sorbents. Some of the researches have obtained rather good results of capacity, but the lack of the discussion of selectivity makes these researches less applicable.

Di-secondary amine types of crosslinked chitosan dibenzo-1-c-6 were prepared by Yi et al. (2003), and the highest uptake of Ag^{+} was found to be 103.68 mg g^{-1} at pH 6.0 and at room temperature with an initial Ag^{+} concentration of 0.5 mmol L^{-1}. However, a monometallic solution containing Ag^{+} alone was used in this study, and the mechanism of the process was not discussed.

Ag^{+}-imprinted epichlorohydrin-crosslinked mycelium-chitosan beads were

established by Huo et al. (2009). The highest uptake of Ag^{+} was found to be 199.2 mg g^{-1} at pH 7.0, with the initial Ag^{+} concentration of 1200 mg L^{-1} and the biosorbent dosage of 3.0 g L^{-1}. Although the uptake appears to be promising, the result was not completely satisfying because a single Ag^{+} solution alone was used in this study and no mechanism was proposed.

Ethylenediamine modified ethylene glycol diglycidyl ether crosslinked chitosan resin was prepared by Elwakeel et al. (2013). The highest uptake of Ag^{+} was found to be 146.88 mg g^{-1} at 25 ℃ . But this study did not discuss the selectivity of the prepared sorbent.

Thiourea/glutaraldehyde grafted magnetic chitosan resin was prepared by Donia et al. (2007). The highest uptake of Ag^{+}, which was obtained at 30 °C and pH 6.9 with the initial concentration of 6 mmol L^{-1}, was 226.8 mg g^{-1}. Although a relatively high capacity was obtained, selectivity was undiscussed.

1.2.3.3. Biosorption of silver ions from bimetallic solutions using chitosan based biosorbents

Ethylenediamine type chitosan resin was successfully developed by Katarina et al. (2006). The highest uptake of Ag^{+} was 39.96 mg mL^{-1} of wet resin at pH 5.0. But the result cannot be used to compare with other references, as mg g^{-1} is the most generally used unit to describe the capacity and the density of the wet resin was not provided. Although the study was conducted with a bimetallic solution containing Ag^{+} and Cu^{2+}, and a possible biosorption mechanism was also presented, the selectivity of the sorbent

was unsatisfactory, as the molar ratio of adsorbed Ag^{+} and Cu^{2+} was 2:1.

Ag^{+}-imprinted epichlorihydrin-crosslinked chitosan was obtained by Song et al. (2012). The highest uptake of Ag^{+} was found to be around 120 mg g^{-1} at natural pH and the biosorbent dosage of 0.4 g L^{-1}. Although the selectivity was not acceptable, this study does provide a theory that a higher imprint ratio may lead to better selectivity.

Tripolyphosphate crosslinked alkalized chitosan beads were synthesized by Mao et al. (2015). The highest uptake of Ag^{+} was 82.9 mg g^{-1} at room temperature with an initial concentration of both Ag^{+} and Cu^{2+} being 2.0 mmol L^{-1} and the sorbent dosage of 1.0 g L^{-1}, the uptake of Cu^{2+} in the sample condition was 15.5 mg g^{-1}. The result of this study is good and the discussion of possible mechanisms was involved. But the capacity of the prepared sorbents, compared with the results of other publications, need to be improved in order to compete with other researches, and the selectivity of the sorbent was unsatisfactory, as the molar ratio of adsorbed Ag^{+} and Cu^{2+} was around 3:1. Furthermore, another disadvantage of this study is that less than 40% of Ag^{+} was adsorbed on the biosorbent.

In summary, some attention has been paid to biosorption of silver using chitosan based biosorbents, but a thorough study which includes all aspects above mentioned is necessary.

1.3. CURRENT WORK

Despite the large number of studies dedicated to the sorption of metal ions by

modified chitosan, most of them have been focused on the evaluation of sorption performances and only a few of them aim at gaining a better understanding of sorption mechanisms. Moreover, the majority of studies in biosorption area deal with the sorption of monometallic system, but research on competitive adsorption from bimetallic or multi-metallic environment is not sufficient. The main topic of the present study is to prepare the modified chitosan biosorbents using crosslinking and ion-imprinting techniques to recover silver ions from the aqueous solution containing silver and copper ions. The objectives of this study are to:

- Prepare chitosan based biosorbents to effectively and selectively recover silver ions from binary metallic systems
- Evaluate the performance of biosorbents prepared under different conditions
- Determine the optimal condition for uptaking silver ions
- Identify the sorption kinetics and equilibrium for the uptake of silver ions
- Explore the possible mechanism for the selectively uptake of silver ions

The scopes of this study are listed as follows:

- Preparation of chitosan based biosorbents for the selective adsorption of Ag^{+} from bimetallic solutions
- Effects of initial pH, initial metal concentration, contact time and temperature on selective sorption of silver ions from the bimetallic solution were studied to determine the optimal condition for the uptake of silver ions
- Different kinetics and isotherm models have been used to describe the

selectively uptake of silver ions on the prepared sorbent

- FTIR and XPS analyses have been applied to verify the selective sorption mechanism of silver ions

The highlighted portion of this study includes:

- Two types of chitosan based biosorbents showed high uptake capacity and extremely good selectivity to Ag^{+} from bimetallic solutions containing the same mole concentration of Ag^{+} and Cu^{2+}
- Imprinting technology, simultaneously with crosslinking, grafting (for ITG-OCMC beads only), has been successfully applied to the sorbent preparation procedure to enhance the selectivity towards Ag^{+}, and the results indicated that the effect of the application of imprinting technology was significant
- The generated chitosan based sorbent beads have relatively consistent shape and size, which make the prepared beads possible to be used in column test of a larger scale
- Many batch experiments and characterization tests provided plenty of experimental data to sum up reasonable inferences of biosorption mechanism
- The generated chitosan based sorbent beads have relatively consistent shape and size, which make the prepared beads possible to be used in column test of a larger scale.

In this thesis, Chapter 1 introduced the background, reviewed the recent research development on the modification methods of biomass for biosorbents, chitosan-based biosorbents and their applications as well as biosorption of silver, and offered the outline of current study. Chapter 2 is the co-authorship statement, which stated the contribution of each co-author to the paper. Chapter 3 mainly discussed the biosorption of silver from bimetallic solutions using the silver ion-imprinted chitosan gel beads. Experimental study of the selective sorption of silver ions using the newly synthesized ion-imprinted thiourea-glutaraldehyde crosslinked O-carboxymethyl chitosan beads was presented in Chapter 4. Major conclusions of this study were summarized and the recommendations for future work were proposed in Chapter 5.

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Chapter 2 Co-authorship Statement

2.1. CO-AUTHORSHIP DECLARATION

I hereby declare that this thesis incorporates material that is the result of joint research, as follows:

After the interest in working in biosorbent preparation and characterization had been expressed by the author, the concept for the project came from thesis co-supervisor Dr. Yan Zhang. More specific ideas were generated by the author during preliminary literature review, and formalized in the form of thesis proposal which were reviewed iteratively by Dr. Yan Zhang. Then, the practical aspects of the research, including the design of the preparation routines, the determination of the experimental variables of biosorbent performance tests, and the selection of proper characterization methods which need to be performed, were organized and finalized by the author and co-supervisor Dr. Yan Zhang, and then executed by the author. Data analysis and manuscripts drafting were also finished by the author. Drs. Yan Zhang and Robert Helleur have paid great efforts to provide guidance in finalizing all practical aspects of the research, coordinating with other groups to provide necessary facilities for experiments and characterizations and critically revising the manuscripts. Besides, Dr. Yan Zhang has provided all the financial support for the whole research.

I am aware of the Memorial University of Newfoundland Senate Policy on Authorship and I certify that I have properly acknowledged the contribution of other

researchers to my thesis, and have obtained permission from each of the co-author(s) to include the above material(s) in my thesis.

I certify that, with the above qualification, this thesis, and the research to which it refers, is the product of my own work.

2.2. DECLARATION OF PREVIOUS PUBLICATION

This thesis includes two original papers that have been previously published/submitted for publication in peer reviewed journals, as follows:

Thesis Chapter	Publication title/full citation	Publication status
Chapter 3	Ion-Imprinted Chitosan Gel Beads for Selective Adsorption of Ag^+ from Aqueous Solutions	Published
Chapter 4	Selective Adsorption of Ag^+ by Ion-Imprinted O-Carboxymethyl Chitosan Beads Grafted with Thiourea-Glutaraldehyde	Published

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Chapter 3

Ion-Imprinted Chitosan Gel Beads for Selective Adsorption of Ag^+ from Aqueous Solutions

In this chapter, ion-imprinted glutaraldehyde-crosslinked chitosan beads have been introduced. The objective of this routine is to prepare a chitosan based biosorbent with only essential modifications, but still has satisfying capacity and selectivity. The main purpose is to provide an applicable but relatively affordable sorbent, which means simplified modifications and minimized dosage of chemical reagents.

The following contents are the same as the manuscript published on *Carbohydrate Polymers* (Volume 130, 5 October 2015, Pages 206-212), except that the removal of the line numbers to maintain the uniform format of the thesis.

3.1. INTRODUCTION

Chitosan is a cationic polysaccharide obtained by partial deacetylation of chitin, the major component of crustacean shells (López-León et al., 2005). Chitosan and its derivatives have been used as antimicrobial agents, biosorbents and polymers for controlled drug release due to their excellent biodegradability, nontoxicity and adsorption properties (Ravi Kumar, 2000; Ghaemy & Naseri, 2012). The presence of amino groups makes chitosan an efficient metal scavenger, capable of retaining metal ions from wastewater (Niu & Voleskey, 2006; Kyzas et al., 2009; Machado et al., 2009; Wan Ngah & Fatinathan, 2010; Vijayaraghavan et al., 2011; Monier, 2012; Zhang et al., 2015). Nevertheless, the poor stability of chitosan in aqueous acidic media restricts its application as a biosorbent, as many industrial effluents tend to be acidic. Chemical modifications of chitosan are thereby essential to improve its chemical stability, mechanical strength and adsorption capacity in acidic media.

Cross-linking has been extensively employed to enhance the chemical stability and mechanical strength of chitosan under acidic environment, but the cross-linked chitosan (in the form of gel beads) usually shows significantly reduced adsorption capacity because of the consumption of the amine groups during the cross-linking reaction (Guibal, 2004; Li et al., 2005; Wan Ngah & Fatinathan, 2010). Moreover, biosorption of industrial effluents is usually carried out under multi-metal ion environment where good selectivity of the biosorbents towards target metal ions is also required. To improve the uptake capacity and sorption selectivity, ion imprinting technology was combined with cross-linking to synthesize the ion-imprinted chitosan beads in the presence of metal ions as templates (Rao et al., 2006; Fan et al., 2011; Liu et al., 2012). The conception of ion-imprinted polymers (IIPs) is very similar to the

molecularly imprinted polymers (MIPs) by changing the template molecule into a metal ion. Imprinting of metal templates is typically achieved by the reduction of receptor mobility through various ways such as bulk polymerization, precipitation polymerization, and suspension polymerization (Branger et al., 2013; Puniredd et al., 2015). Ion imprinting technology is very efficient in generating recognition sites and has been successfully applied to different polymers, for example, chitosan (Tao et al., 2013), poly(ethylene terephthalate), polyazomethine amides (Monier & Abdel-Latif, 2013) for the selective uptake of different kinds of metal ions, such as Ag, Cu, Hg, As, Pb, Cd, Ni, Zn and Co (Li et al., 2005; Chen et al., 2011; Fan et al., 2011; Murugesan et al., 2011; Liu et al., 2012; Nishad et al., 2012; Monier & Abdel-Latif, 2013).

Biosorption is a physicochemical and metabolically-independent process, involving different sorption mechanisms (Fomina & Gadd, 2014; Won et al., 2014). It is important to unearth the real sorption mechanism because it enables the possibility for further improving the biosorption performance (e.g., capacity, selectivity and adsorption rate). To date, the binding mechanism of metal ions to chitosan based sorbents is not yet fully understood. Various processes such as electrostatic attraction, ion exchange, and complexation/chelation are discussed as the potential mechanisms (Guibal, 2004). Electrostatic attraction arises when sorbent surfaces are charged with different signs of metal ions. Metal uptake through biosorption also takes place due to the exchange of protons with metal ions when the solution pH ranges between 2 to 4 (Donia et al., 2007; Quignard et al., 2010; Chen et al., 2011). Complexation/chelation is based on coordination chemistry, which refers to the ability of metal ions to interact or enter into coordinate bonding with other ions or ligands (Guibal, 2004). X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy

are extensively utilized to provide insight into the metal binding process at the molecular level (Dambies et al., 2001; Lim et al., 2008).

In this study, the silver ion-imprinted chitosan gel beads were prepared to selectively adsorb Ag^+ from bimetallic solutions containing equal moles of Ag^+ and Cu^{2+}. Characterization of the imprinted sorbent, effects of initial pH, initial metal concentration and contacting time on the selective adsorption of Ag^+ were investigated. The adsorption isotherm and kinetic parameters were also determined by tuning various models with the experimental measurement. Finally the selective adsorption mechanism of Ag^+ by the synthesized gel beads was elucidated via FTIR in combination with XPS analyses. Silver is a very important industrial metal, it is usually distributed with low contents in copper ores. Appreciable amounts of Ag^+ and Cu^{2+} coexist in the mining wastewater. Development of a cost-effective biosorption process to recover silver from dilute waste solutions is important from both economic and environmental perspectives.

3.2. MATERIALS AND METHODS

3.2.1. Materials

Chitosan with 80 meshes, 91.03% degree of deacetylation and molecular weight in the range of 100-300 kDa was purchased from Fisher Scientific. Acetic acid, sodium hydroxide, formaldehyde, glutaraldehyde, acetone, sulphuric acid, thiourea, silver nitrate and copper nitrate were purchased from Fisher Scientific as well and used without further purification. The deionized water was generated from Milli-Q water purification system in the lab.

3.2.2. Preparation of the Ag^+-imprinted chitosan gel beads

The Ag^+-imprinted chitosan gel beads were prepared in four major steps, including immobilization of chitosan beads, Ag^+ template imprinting, cross-linking and removal of the template. In this study, glutaraldehyde and formaldehyde, the commonly used fixatives were selected as the cross-linking agents. In both cases, chitosan is crosslinked by the Schiff base mechanism, in which the aldehyde groups react with the primary amine groups of chitosan, leading to the formation of imine bonds (Wan Ngah & Fatinathan, 2008). The only difference lies in the imine bond is stabilized in case of glutaraldehyde crosslinking, whereas the imine bond is further reduced to the C-N bond (amine) via hydrogenation during the formaldehyde crosslinking of chitosan (Singh et al., 2006).

To investigate the effectiveness of the ion-imprinted in enhancing the selectivity and capacity of sorbents, chitosan gel beads without Ag^+ imprinting were also prepared for comparison.

3.2.2.1. Preparation of Chitosan Beads

5.000 wt% chitosan beads, 1.2~1.5 mm in diameter, were prepared using the methods described by Wan Ngah and co-workers (Wan Ngah & Fatinathan, 2008). 5.0000 g of chitosan powder was dissolved in 100.0 mL of 5 wt% acetic acid; the mixture was left overnight to obtain a homogeneous chitosan solution before being added dropwise into 500.0 mL of 0.5000 M NaOH solution. The NaOH solution was under a continuous stirring at 150 rpm for 24 h to coagulate spherical chitosan beads and to neutralize the acetic acid within the beads. The chitosan beads were filtered,

rinsed with deionized water, and then stored in deionized water for use.

3.2.2.2 Imprinting

Wet chitosan beads were added into 200.0 mL of 10.00 mmol L^{-1} silver nitrate solution, shaking at 150 rpm for 48 h. The beads were filtered and excess Ag^{+} was removed by rinsing with deionized water, and then stored in deionized water for use.

3.2.2.3 Cross-linking

Different amounts of cross-linking agent solutions were added dropwise into flasks containing 1.0000 g of Ag^{+}-imprinted chitosan beads and 100.0 mL deionized water. The cross-linking reaction lasted 24 h with constant shaking at 150 rpm. The synthesized chitosan gel beads were filtered and washed in sequence with dilute sodium hydroxide, deionized water, and finally acetone. The beads were air dried for 48 h to remove the acetone and then stored in deionized water.

3.2.2.4 Removal of the template

Water solution containing 3.500 wt% of thiourea and 0.07500 vol% of H_2SO_4 was used to remove the template Ag^{+} from the synthesized chitosan gel beads. The mixture was under constant shaking at 150 rpm for 24 h. After desorption, the regenerated beads were filtered and rinsed with deionized water, air-dried for 48 h and finally stored in sealed bottles until use.

3.2.3. Batch Sorption Experiments

Bimetallic solutions containing equal moles of Ag^{+} and Cu^{2+} ions were prepared from the standard 100.0 mmol L^{-1} silver nitrate and copper nitrate solutions for all the

sorption experiments. The effects of pH (1.0 – 5.0), sorbents prepared under different conditions, initial metal concentration (0.2500 – 3.300 mmol L^{-1} each metal ion) and contact time (1 – 48 h) on selective adsorption of Ag^{+} were investigated. The experiments were performed at 25.0 °C by mixing 100.0 mg synthesized chitosan gel beads with 100.0 mL (150.0 mL for kinetic experiment) of bimetallic solutions in 250.0 mL Erlenmeyer flasks under the constant shaking at 150 rpm. Samples of 3.0 mL solution were collected at the end of experiments and filtered for concentration measurement by ICP-OES. The amount of adsorption, q_i (mg g^{-1}) for of each metal ion ($i = Ag^{+}$ or Cu^{2+}) was calculated by Eq.3-1 listed as below:

$$q_i = \frac{(c_{i,0} - c_{i,e})V}{W} \qquad \text{Eq. (3-1)}$$

where $c_{i,0}$ and $c_{i,e}$ (mg/L) are the initial and final concentrations of metal ion i in the solution; V (L) is the volume of bimetallic solution and W (g) is the weight of the dry sorbent.

Bimetallic solution with initial concentration of 1.000 mmol/L for each metal ion was used for the kinetic experiment. Samples of 3.0 mL solution were withdrawn at the scheduled time interval and filtered for later concentration measurement by ICP-OES. The uptake of Ag^{+} and Cu^{2+} at different sampling points can be calculated by Eq. 3-2.

$$q_{i,j} = \frac{(c_{i,0} - c_{i,j})V - V_s\left(\sum_{k=1}^{j} c_{i,k} - jc_{i,j}\right)}{W} \qquad \text{Eq. (3-2)}$$

where $q_{i,j}$ (mg/g) is the amount of metal ion i adsorbed at sampling point j ($j \geq 1$); $c_{i,j}$ (mg/L) is the concentration of metal ion i in the aqueous solution at sampling point j; V and V_s (L) are the initial solution volume and the sampling volume respectively; W (g) is the weight of the dry sorbent.

3.2.4. Analytical methods

The pH value of sample solutions was measured by an Accumet pH meter, AB 15^{+} (Fisher Scientific, Canada). Perkin Elmer Optima 5300DV (Perkin Elmer, Canada) inductively coupled plasma optical emission spectrometer (ICP-OES) was used to determine the concentration of metal ions. Standard solutions containing 0.00, 0.01, 0.10, 1.00 and 10.00 mg/L Ag^{+} and Cu^{2+} in 2% HNO_3 were used to get the calibration curves. Yttrium (10.00 mg/L) was used as an internal standard. Sample solutions were diluted 20 times with 2% HNO_3 solution for the ICP-OES measurement. Analysis on Ag^{+} was conducted at wavelengths of 338.290 nm, 328.068 nm and 243.774 nm, analysis on Cu^{2+} was performed at wavelengths of 327.393 nm, 324.755 nm and 224.698 nm. Reported values were the mean of three consecutive replicate measurements and were corrected for dilution.

The Fourier transform infrared (FTIR) spectra of Ag^{+}-imprinted chitosan gel beads before and after metal uptake were recorded by a Tensor 27 FTIR spectrometer (Bruker, Germany). All samples were prepared as KBr pellets and scanned in the wavenumber range of 400-4000 cm^{-1} at room temperature. X-ray photoelectron spectra of IGCC beads were obtained on an AXIS 165 X-ray photoelectron spectrometer (Kratos Analytical, USA) with Al Kα X-ray source.

3.3. RESULTS AND DISCUSSION

3.3.1. Sorbent Screening

The adsorption performance of the chitosan gel beads prepared under different conditions is summarized in Table 3.1. Results from Table 3.1 reveal that cross-linked

chitosan beads with or without Ag^+-imprinting both show the extremely good selectivity towards Ag^+, indicating that Cu^{2+} is not capable of competing with Ag^+ for the available amine binding sites. The main cause is that Cu^{2+} is more electropositive than Ag^+ and more electron-donoting atoms need to be involved in binding Cu^{2+}, making Cu^{2+} inferior to Ag^+ in the competition of binding sites. In addition, gel beads prepared with Ag^+-imprinting have much higher uptake capacities than those without Ag^+-imprinting. This is because that Ag^+-imprinting of chitosan before crosslinking protects some amine groups, the primary binding sites of metal ions from crosslinking, leading to an increased number of binding sites and thus a higher Ag^+ uptake capacity.

Results from Table 3.1 also indicate that degree of crosslinking shows divergent influences on the amount of Ag^+ uptake by sorbents prepared with and without ion-imprinting. It is clearly seen that regardless of the type of crosslinking agents low degree of crosslinking helped to obtain high capacity sorbents when ion-imprinting was not applied during sorbent preparation. This is reasonable as more binding sites on chitosan are preserved at lower degree of crosslinking. Nonetheless, in case of ion-imprinting, the amount of Ag^+ uptake increases with the increasing crosslinking with both glutaraldehyde and formaldehyde. This result indicates that the increased amount of crosslinking agents made the reactions between Ag^+ bound chitosan and crosslinking agents more complete and the volumetric density of Ag^+ bound sites increased. Therefore, after removal of the template Ag^+ ions, an improvement of volumetric sorption capacity was obtained for the prepared gel beads.

In this study, gel beads cross-linked with formaldehyde and glutaradehyde demonstrate very close sorption performance. Because formaldehyde is more toxic,

glutaraldehyde was selected as the cross-linking agent to synthesize the Ag^+-imprinted chitosan gel beads. The highest selective uptake of Ag^+ (46.30 mg g^{-1}) occurred when 2: 1 molar ratio of the aldehyde groups of glutaraldehyde to the amino groups of chitosan (No.1 in Table 3.1) was used. Thereby, the Ag^+-imprinted glutaraldehyde cross-linked chitosan (IGCC) beads prepared under this condition was chosen for further experimental investigation.

Table 3.1. Adsorption* of Ag^+ and Cu^{2+} on chitosan gel beads prepared under different conditions

No.	Cross-linking agent	n(CHO):n(NH_2) †	Imprinted or Not	q_{Ag} mg g^{-1}	q_{Cu} mg g^{-1}
1	$CH_2(CH_2CHO)_2$	2:1	Y	46.30	0.72
2	$CH_2(CH_2CHO)_2$	2:1	N	19.15	0.93
3	$CH_2(CH_2CHO)_2$	1:1	Y	36.86	0.19
4	$CH_2(CH_2CHO)_2$	1:1	N	21.70	0.76
5	CH_2O	0.22:1	Y	44.54	0.74
6	CH_2O	0.22:1	N	15.05	1.19
7	CH_2O	0.11:1	Y	41.65	0.81
8	CH_2O	0.11:1	N	20.75	1.08

Note: * Batch sorption experiment for sorbents screening was performed for 24 h.

† The molar ratio of CHO:NH_2 was selected based on the values reported in the literature (Wan Ngah & Fatinathan, 2008; Du et al., 2009).

3.3.2. Characterization of IGCC beads

Fig. 3.1 shows the FTIR spectra of chitosan powder and IGCC beads. The characteristic peaks of chitosan powder are: 3448.59 cm^{-1} corresponding to –NH and –OH stretching vibration; 1653.94 cm^{-1} due to –NH deformation vibration; 1154.29 cm^{-1}

for –CN stretching vibration and 1078.83 cm^{-1} due to stretching vibration of –C-OH (Li & Bai, 2005). Structural changes of IGCC beads before metal uptake were confirmed from their FTIR spectra. The –NH and –OH stretching vibration peak was shifted to 3440.44 cm^{-1} in the spectrum of IGCC, -NH deformation vibration peak was shifted to 1631.50 cm^{-1}, as a results of the amino and hydroxyl groups of chitosan being substituted. Peak at 1078.83 cm^{-1} only shifted for 2.63 cm^{-1} to 1081.46 cm^{-1}, which may be considered as insignificant variations. Together with the peak shift from 1154.29 cm^{-1} to 1164.48 cm^{-1}, the cross-linking reaction could be confirmed to have taken placed on –C-NH_2 (Tsezos, et al., 1996).

XPS was also used to characterize the surfaces of IGCC beads. The XPS survey spectrum of IGCC beads before metal uptake is shown in Fig. 3.2. Binding energy (BE) peaks at 285.4 eV for C 1s, 531.8 eV for O 1s and 401.0 eV for N 1s are clearly visible, among which the O 1s peak at 531.8 eV is assigned to O=C, indicating glutaraldehyde was grafted onto chitosan. The peak at 167.8 eV is assigned to S atom in -SO_x (contaminated S) due to the use of sulfuric acid in removing the template Ag^+ from IGCC beads.

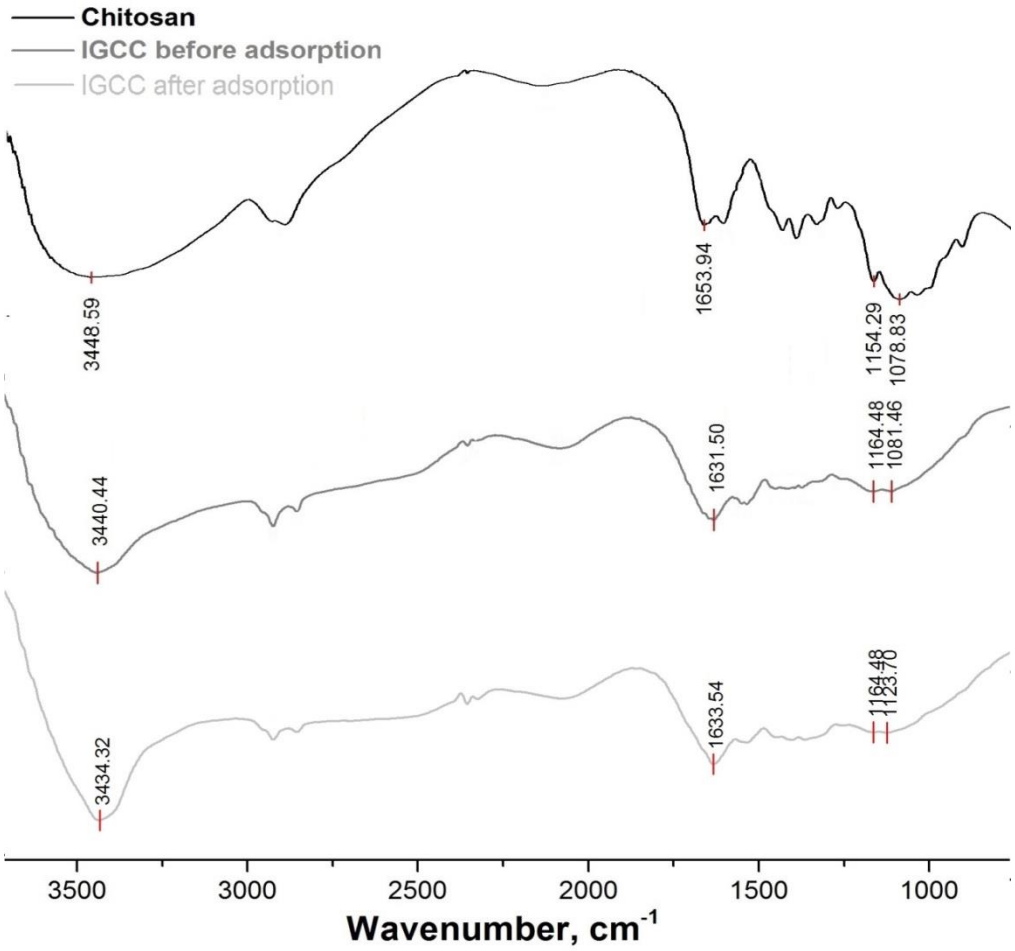

Fig. 3.1. IR spectra of chitosan, and IGCC beads before and after metal uptake

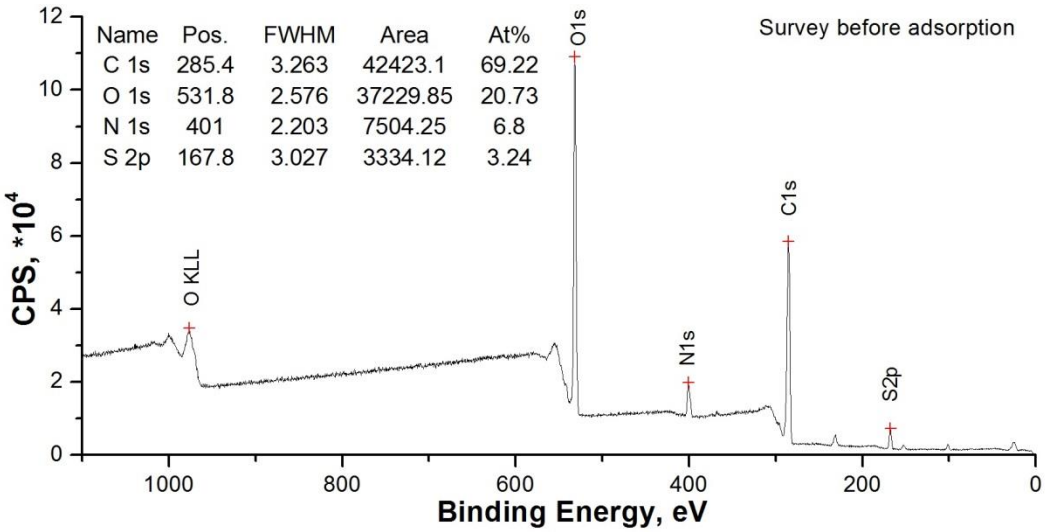

Fig. 3.2. XPS survey spectrum of IGCC beads

3.3.3. Effect of pH

The effect of the initial solution pH on the uptake of Ag^{+} and Cu^{2+} by the IGCC gel beads was studied and the results are illustrated in Fig. 3.3. The uptake of Cu^{2+} by IGCC beads was very low over the entire pH range, with the highest uptake of 1.7 mg g^{-1} sorbent at pH 1.0. The uptake of Ag^{+} demonstrates a "V" shaped curve, with the adsorption amount of Ag^{+} being the lowest at pH 3.0. In the pH range of 1.0 - 3.0, most of the free amine groups of IGCC beads are protonated, the uptake of Ag^{+} decreases with the reducing number of protonated amine groups, indicating that Ag^{+} was bound to IGCC through the exchange of protons. However, at pH > 3.0, the uptake of Ag^{+} increases with the increasing solution pH, suggesting the binding of Ag^{+} to sorption sites is mainly through complexation interaction because the number of free amine groups increases synchronously with the solution pH. Compared with the uptake of Ag^{+} at pH 1.0, the adsorption amount of Ag^{+} at pH 5.0 is slightly (≈1.0 %) lower. However, the pH of the bimetallic solution containing equal moles of Ag^{+} and Cu^{2+} is close to 5.0, and as such, further sorption tests were conducted without adjusting the pH of the bimetallic solution.

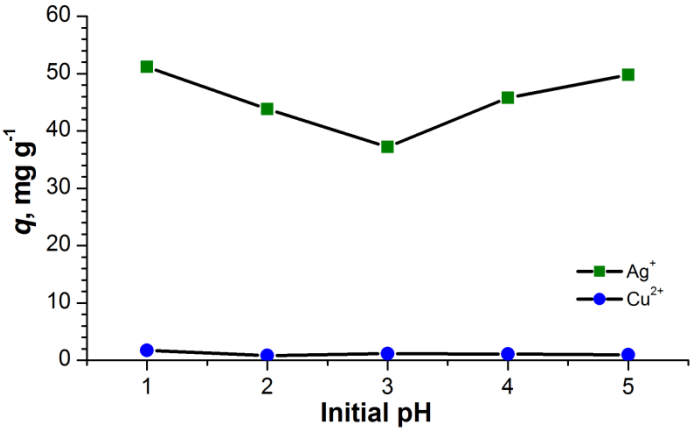

Fig. 3.3. Effect of pH on the uptakes of Ag^{+} and Cu^{2+}

3.3.4. Adsorption kinetics of Ag^+

The effect of contact time on the selective sorption of Ag^+ was demonstrated in Fig. 3.4. As Cu^{2+} is scarcely (< 2.0 mg g^{-1} sorbent) adsorbed by the IGCC beads, kinetic and isotherm studies of Cu^{2+} adsorption were not presented hereinafter. Results from Fig. 3.4 demonstrate adsorption of Ag^+ by IGCC beads in general is quite slow. IGCC binding of Ag^+ kept on increasing and adsorption equilibrium was not completely achieved after 48 h due to the low mass transfer rate of metal ions in the IGCC gel beads.

Several adsorption kinetic models can be applied to interpret the adsorption kinetics and the rate limiting step during adsorption. The pseudo-first and -second order equations are mainly applied in the biosorption with sharing or exchange of electrons between functional groups and metal ions (Ho, 2006). The intraparticle diffusion model which highlights the importance of mass transfer in the hydrogel beads has also been successfully applied to describe the sorption kinetics of metal ions (Wan Ngah, & Fatinathan, 2010). In addition, Elovich equation (Chien & Clayton, 1980) which assumes the adsorption occurred on the heterogeneous surface usually provides accurate explanations of the slow biosorption kinetics. All the four rate equations were employed to quantify the time effect on the uptake of Ag^+ by the IGCC beads. The rate equations of the four different models are listed below.

Pseudo-first order equation:

$$q_t = q_e(1 - \exp(-k_1 t)) \qquad \text{Eq. (3-3)}$$

Pseudo-second order equation:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$ Eq. (3-4)

The intraparticle diffusion model:

$$q_t = k_m t^{1/2}$$ Eq. (3-5)

And the Elovich rate equation:

$$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t$$ Eq. (3-6)

where q_e and q_t (mg/g) are the amounts of Ag^+ adsorbed by IGCC at equilibrium and at time t, respectively, and k_1 (h^{-1}) is the rate constant of pseudo-first order kinetic model; k_2 (g mg^{-1} h^{-1}) is the rate constant of second-order kinetic model; k_m (mg g^{-1} $h^{-0.5}$) is the intraparticle diffusion constant; while α (mg g^{-1} h^{-1}) and β (g mg^{-1}) are the initial adsorption and desorption rate constants for Elovich rate equation, respectively.

The kinetic parameters for the different rate equations were determined by linear and nonlinear curve fittings using MATLAB R2012a and the results are listed in Table 3.2. The measured kinetic data and the model predicted kinetic results are compared and illustrated in Fig. 3.4. It was found that pseudo-first order and intraparticle diffusion models gave better correlations than the pseudo-second order and Elovich rate equations for the sorption of Ag^+.

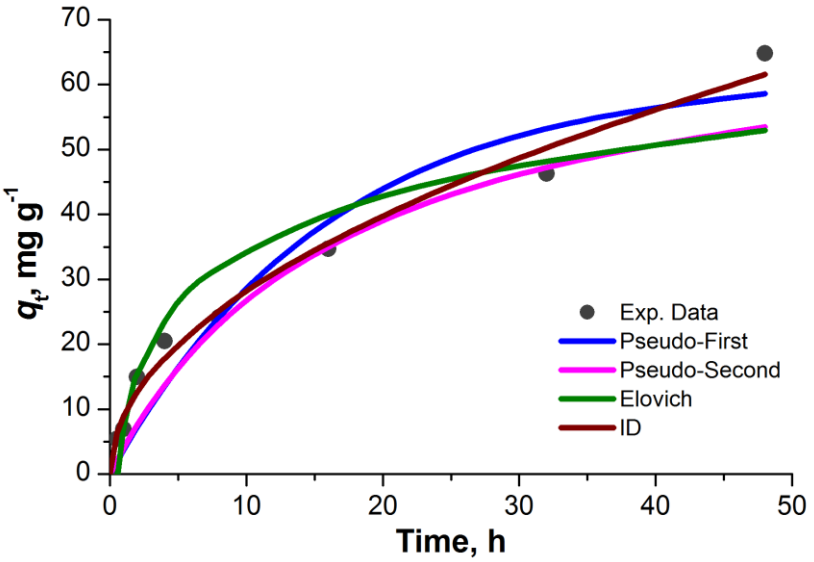

Fig. 3.4. Adsorption kinetics of Ag^+ at 25.0°C with initial concentrations of 1.0000 mmol L^{-1}

Table 3.2 Kinetic parameters for Ag^+ adsorption on IGCC beads

Kinetic Equation		Rate Parameters
Pseudo-first order		
k_1	h^{-1}	6.20×10^{-2}
q_e	mg g^{-1}	61.74
R^2		0.934
Pseudo-second order		
k_2	g mg^{-1} h^{-1}	8.0×10^{-4}
q_e	mg g^{-1}	77.64
R^2		0.910
Intraparticle diffusion		
k_m	g mg^{-1} $h^{-0.5}$	8.887
R^2		0.984
Elovich		
α	mg g^{-1} h^{-1}	21.61
β	g mg^{-1}	8.44×10^{-2}
R^2		0.894

3.3.5. Adsorption isotherm of Ag^+

The effect of initial concentration on the adsorption equilibrium of Ag^+ was demonstrated in Fig. 3.5. It is observed that equilibrium uptake capacity of Ag^+ increases when the initial concentration of Ag^+ raised from 0.2000 to 3.300 mmol L^{-1}; the uptake capacity remain constant when the initial concentration is higher than 3.300 mmol L^{-1}.

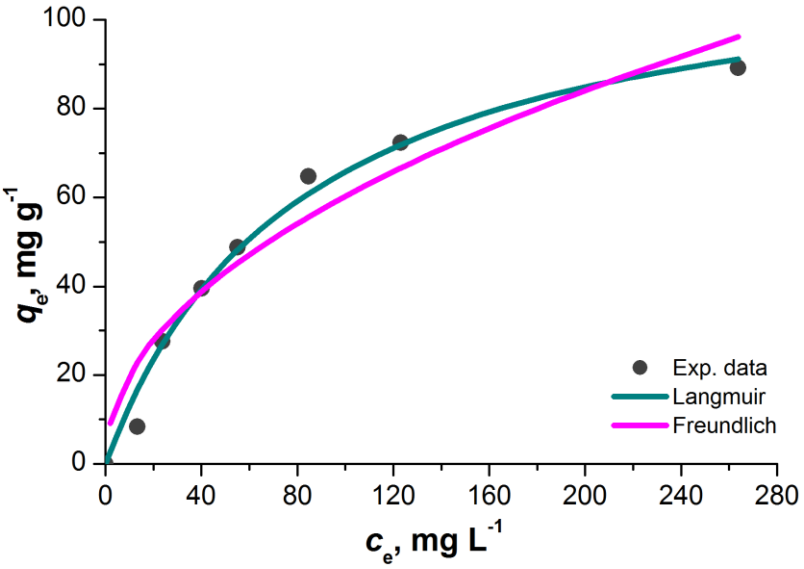

Fig. 3.5. Adsorption isotherm of Ag^+ at 25.0 °C

Langmuir and Freundlich isotherm models (Ruthven, 1984) given in Eqs.3-7 and 3-8 were used in this study to explicate the adsorption equilibrium of Ag^+ on IGCC beads.

$$q_e = \frac{q_s b c_e}{1 + b c_e} \qquad \text{Eq. (3-7)}$$

$$q_e = K_F c_e^{1/n} \qquad \text{Eq. (3-8)}$$

where q_e (mg g^{-1}) is the amount of Ag^+ adsorbed at equilibrium, c_e (mg L^{-1}) is the

equilibrium concentration of Ag^+ in solution, q_s (mg g^{-1}) is the maximum biosorption capacity, b is the sorption equilibrium constant, K_F is a constant indicative of the adsorption capacity of the sorbent, and $1/n$ is a measure of adsorption intensity.

Similarly, MATLAB R2012a was used to determine the isotherm parameters of Langmuir and Freundlich models and the obtained model parameters are listed in Table 3.3. Both models provide accurate sorption equilibrium of Ag^+, well in agreement with the measured data as illustrated in Fig. 3.5. Results from Table 3.3 and Fig. 3.5 indicate that Langmuir isotherm delineates the experimental data better than Freundlich model. Both Langmuir and Freundlich models are favourable type of isotherm, indicating that IGCC beads are very effective in retaining Ag^+ from dilute solutions.

Table 3.3 Isotherm parameters for Ag^+ adsorption on IGCC beads

T	**Langmuir**			**Freundlich**		
K	b L mg^{-1}	q_s mg g^{-1}	R^2	K_F	n	R^2
298.15	1.23×10^{-2}	119.25	0.977	6.573	2.078	0.902

3.3.6. Selective sorption mechanism

To disclose the potential selective sorption mechanism, FTIR analysis of IGCC beads after metal uptake was carried out and results can be found in Figs. 3.1. The IR spectrum of IGCC after metal uptake is almost identical to that before adsorption, which indicates that the chemical structure of IGCC beads was not significantly changed after adsorption of Ag^+ ions. But a reduction in the peak intensity was observed between 1000 cm^{-1} and 1300 cm^{-1}, which can be assigned to –NH deformation

vibration and stretching vibration of –C-OH (Baroni et al., 2008). In addition, peak shift of the –NH and –OH stretching vibration from 3440.44 cm^{-1} to 3434.32 cm^{-1} suggests the binding of Ag^{+} to amine and hydroxyl groups.

XPS analysis of the IGCC beads after metal uptake was also conducted to examine the selective adsorption mechanism. The survey spectrum shown in Fig. 3.6 indicates the presence of carbon, oxygen, nitrogen, and silver. The photoemission bands Ag3d, Ag3p1, and Ag3p3 showed that a significant amount of Ag has been adsorbed. Furthermore, based on the high resolution spectra, the doublet of Ag3d in Fig. 3.7a is assigned to compounds formed between N and Ag. The BE shift is only 0.2 eV after metal uptake (Fig. 3.7b) although the intensity of the peak increases significantly. This result suggests that a significant amount of Ag^{+} is bound to the sites which are previously occupied by the template Ag^{+}.

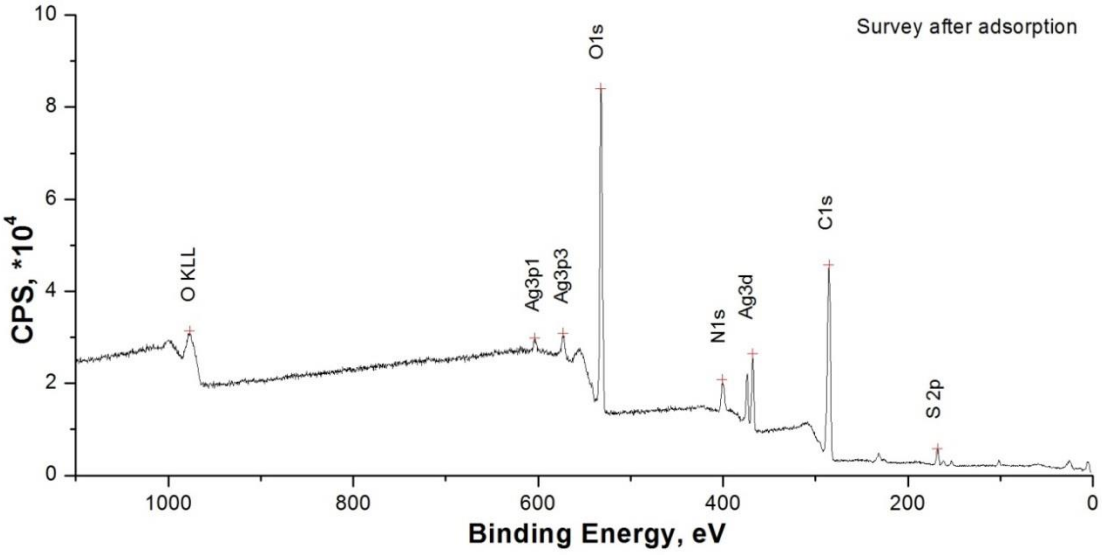

Fig. 3.6. XPS survey spectrum of IGCC beads after metal sorption

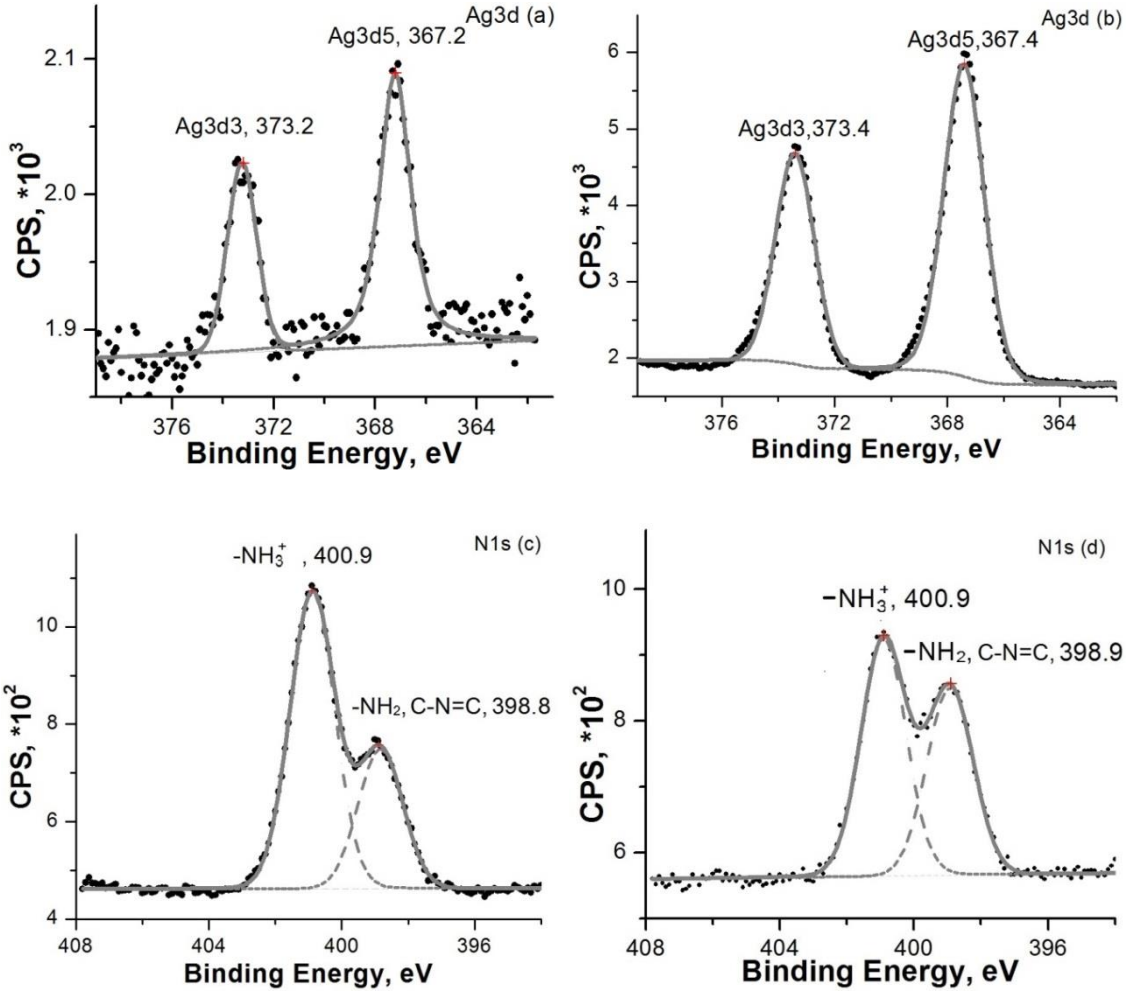

Fig. 3.7. Fitted high-resolution photoemission spectra of Ag 3d, and N1s before (a), (c) and after (b), (d) metal uptake for IGCC beads. Label: (•) recorded signals; (—) Voigt-type fitted curves; and (- -) deconvoluted regions from the fitted curves.

High resolution XPS spectra of N 1s of the sorbent before and after metal uptake are compared in Figs. 3.7c-3.7d. Two BE peaks at 398.8 and 400.9 eV are visible for N 1s spectrum before sorption. According to Moulder et al., (Moulder et al., 1992), N 1s peak at 398.8 eV was assigned to free amine group ($–NH_2$) and C=N-C whereas the higher BE peak at 400.9 eV was assigned to the protonated amine group ($-NH_3^+$). After metal adsorption, N 1s peak at 398.8 eV shifted to 398.9 eV, indicating the formation of

$R\text{-}NH_2Ag^+$ complexes, in which the lone pair electrons from the N atoms interacted with the Ag^+, and hence the electron cloud density of the nitrogen atom was reduced, resulting in a slightly higher BE peak. XPS results of IGCC before and after metal uptake disclose that amine group provides the primary binding sites for Ag^+.

3.4. CONCLUSIONS

The selective biosorption of Ag^+ from equal molar Ag^+ and Cu^{2+} solutions was investigated using Ag^+-imprinted glutaraldehyde cross-linked chitosan (IGCC) beads. Results indicated that IGCC gel beads provide superb selectivity towards Ag^+ over the entire pH range ($1.0 \leq pH \leq 5.0$) studied, regardless of the initial metal ion concentration. The maximum uptake of Ag^+ is 89.200 mg g^{-1}sorbent at 25.0 °C. Although favourable isotherm type was observed for the sorption process of Ag^+ on the imprinted sorbent, the sorption rate of Ag^+ was slow. Further analyses from FTIR and XPS revealed that amine functional groups contribute to the binding of Ag^+ via complexation at higher solution pH ($3.0 \leq pH \leq 5.0$) and ion exchange at lower solution pH ($1.0 \leq pH < 3.0$).

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Chapter 4

Selective Adsorption of Ag^+ by Ion-Imprinted O-Carboxymethyl Chitosan Beads Grafted with Thiourea-Glutaraldehyde

In this chapter, ion-imprinted thiourea-glutaraldehyde-grafted O-carboxymethyl chitosan beads have been introduced. The objective of this routine is to obtain a chitosan based biosorbent which has relatively high capacity, selectivity, and reusability. A novel technique which combines the metal ion-imprinting, grafting and crosslinking was applied to achieve the goal in this study.

The following contents are the same as the manuscript published on *Chemical Engineering Journal* (Volume 264, 15 March 2015, Pages 56-65), except that the format of the references has been modified to maintain the uniform format of the thesis.

4.1. INDRODUCTION

Biosorption, which was defined by most researchers as a passive and metabolically-independent process, has been recognized as an effective method for the removal or concentration of metals from solutions (Volesky, 2007; Gadd, 2009; Das, 2010; Kotrba, 2011). Biosorbents prepared from agricultural wastes, industrial wastes, and natural residues have been widely used to retain/remove heavy metals from wastewater due to their biodegradable, biocompatible, renewable and nontoxic nature (Volesky and Holan, 1995). Among the huge biomass resource pool, chitosan, a biopolymer obtained from the deacetylation of chitin, has been identified as an efficient metal scavenger due to the presence of reactive amino groups. Grafting new functional groups on the chitosan backbone was also reported to be efficient in increasing either the sorption capacity or sorption selectivity for the target metal (Guibal, 2004; Fan et al., 2011). However, the dissolution of chitosan in dilute acid has limited its application as a sorbent, as many industrial effluents tend to be acidic. Moreover, powder form of chitosan is not suitable to be packed in a column for applications at preparative scale because they may cause clogging problems, a huge pressure drop or serious hydrodynamic limitations. Gel beads are regarded as the best form of biopolymer based sorbents for metal uptake from aqueous solution (Guibal, 2004). It is therefore of uttermost importance to physically or chemically modify chitosan powders for practical implementations.

Crosslinking has long been used to improve the chemical resistance of chitosan in acidic media, but when amino groups are involved in chemical crosslinking process, the uptake capacity of chitosan decreases (Wan Ngah and Fatinathan, 2010). To improve

the capacity, grafting of certain function groups is necessary before crosslinking (Donia et al., 2008). Carboxymethyl chitosan (CMC), which has amino group, carboxyl group, and hydroxyl groups at C-2 and C-3 position, can enhance the sorption capacity with various metal ions (Hon and Tang, 2000; Chen and Park, 2003; Choong and Wolfgang, 2003), and the preparation procedure is considered to be simple and efficient. Precious metal ions have a preference for complexion with ligands with more electronegative donor atoms, such as N and S, based on the theory of hard and soft acids and bases (HSAB) theory defined by Pearson (Zhou et al., 2009). Thiourea contains both N and S groups; therefore, thiourea modification of CMC has the potential to increase the uptake capacity towards precious metals (Guibal et al., 2001; Chen et al., 2005).

Surface imprinting technology has attracted much attention in generating recognition sites, and has been successfully applied to prepare metal ion imprinted polymers through the use of various templates (Fan et al., 2011; Branger et al., 2013). The coordination between the imprint ions and the monomers can be based on non-covalent interactions, such as hydrogen bonds, electrostatic interactions, hydrophobic effects, Van der Waals forces, etc., or reversible covalent bonds (Rao et al., 2006). This technology has been successfully applied to different polymeric materials, such as chitosan (Chen et al., 2011), poly(ethylene terephthalate) and polyazomethine amides (Monier and Abdel-Latif, 2013) for the uptake of different kinds of target metal ions, such as Ag, Cu, Hg, As, Pb, Cd, Ni, Zn and Mn (Li et al., 2005; Guan et al., 2008; Chen et al., 2011; Fan et al., 2011; Murugesan et al., 2011; Liu et al., 2012; Monier and Abdel-Latif, 2013).

So far, most of the studies in biosorption area focused on the sorption of monometallic system. A major complication in the application of biosorption to

industrial conditions is the presence of other metal ions in the wastewater to be treated. The effect of the co-existing metal ions on the selective adsorption of the meal of interest may be different under different scenarios. Usually, the co-existing metals ions compete with the metal ion of interest for binding sites and thus lower the specificity of the biosorbent (Mack et al., 2007). However, it is also reported that the presence of a hard acid had no effect on the biosorption of a soft acid (Tsezos et al., 1996). Usually, a variety of metal ions coexists in industrial effluents; study the selective biosorption of a specific metal ion from multi-metal ion environment is more important and valuable.

A novel technique which combines the metal ion-imprinting and crosslinking was applied to synthesize the Ag^{+}-imprinted thiourea/glutaraldehyde modified O-carboxymethyl chitosan (ITG-OCMC) beads in this study. The newly synthesized beads were used to selectively adsorb Ag^{+} from a bimetallic solution containing equal moles of Ag^{+} and Cu^{2+}. Silver and copper are very important industrial metals, extensively used in the fields of aerospace, electroplating and electrical industries due to their excellent malleability and extremely high electrical conductivity. Silver has been found to be widely distributed with low contents in copper ores. Appreciable amounts of Ag^{+} and Cu^{2+} coexist in wastewater from mining and mineral processing. Development of novel and cost-effective technology to isolate Ag^{+} and Cu^{2+} from dilute aqueous solutions is important from both economic and environmental perspectives.

In the current study, optimal conditions for the sorbent preparation has been determined by varying the amount of carboxymethylation agent, the amount of Schiff's base agent and the use of imprinting technology. Effects of initial pH, initial concentration, contact time and temperature on selective sorption of Ag^{+} from

bimetallic solution were also studied. Different kinetics and isotherm models have been used to describe the selectively Ag^+ uptake on the prepared sorbent. FTIR and XPS analyses have been applied to disclose the selective sorption mechanism of Ag^+. The reusability of the prepared sorbent was also investigated.

4.2. MATERIALS AND METHODS

4.2.1. Materials

Chitosan with 80 mesh, 91.03% degree of deacetylation and average molecular weight of 2×10^5 g mol^{-1} was purchased from Fisher Scientific. Acetic acid, sodium hydroxide, monochloroacetic acid, isopropanol, ethanol, hydrochloric acid, thiourea, glutaraldehyde, acetone, silver nitrate, sulfuric acid, copper nitrate were purchased from Fisher Scientific as well and used without further purification. The deionized water, generated from Milli-Q water purification system was used as the solvent for solution preparation. As one of the primary objectives of this study is to explore the selective sorption mechanism of bimetal ions, the use of natural water or wastewater in solution preparation makes the investigation of sorption mechanism much more difficult due to the presence of all types of impurities.

4.2.2. Preparation of ITG-OCMC beads

Four major steps, including carboxymethylation of chitosan beads, surface silver imprinting, crosslinking with thiourea/glutaraldehyde and regeneration of the imprinted biosorbent were involved in synthesizing the novel ITG-OCMC beads. The thiourea/glutaraldehyde grafted CMC beads without surface imprinting (TG-OCMC) were also prepared for comparison.

4.2.2.1. Preparation of OCMC Beads

5.000 wt% chitosan beads, 1.2~1.5 mm in diameter, were prepared using the methods described by Wan Ngah and co-workers (Wan Ngah and Fatinathan, 2008). Two types of OCMC beads were obtained by O-carboxymethylating chitosan beads with varying amounts (Table 4.1) of 37.50 wt% monochloroacetic acid/isopropanol solution. In this process, wet chitosan beads (containing 5.0000 g dry basis of chitosan) were first immersed in 100.0 mL of 1.690 mol L^{-1} NaOH solution to swell and alkalize for 12 h. Monochloroacetic acid/isopropanol solution was then added drop-wise into the flask containing alkalized chitosan beads over 30 min. The reaction lasted 4 hours at room temperature and was stopped by adding 200.0 mL of 70% ethanol. The mixture was filtrated to remove the solvent and the acquired Na salt OCMC beads were rinsed with 70% ethanol. The H-form OCMC beads were prepared by suspending the Na salt OCMC beads into a solvent consisting of 100.0 mL of anhydrous ethanol and 50.0 mL of 37% hydrochloric acid for 1 h. H-form OCMC beads were stored in 70% ethanol after filtration and rinsing.

4.2.2.2 Surface imprinting

Wet H-form OCMC beads were added into 200.0 mL of 10.00 mmol L^{-1} silver nitrate ethanol solution, shaking at 150 rpm for 24 h. The beads were filtered and excess Ag^{+} was removed by rinsing with 70% ethanol, and then stored in 70% ethanol for use.

4.2.2.3 Crosslinking

1.5000 g of thiourea was dissolved in 30.0 mL of deionized water. The thiourea solution was then mixed with 8.5 mL of 50.00 wt% glutaraldehyde in a flask. The

mixture was heated in an incubator to 50 °C, shaking at 150 rpm for 3 h. Different amounts (Table 4.1) of Ag^+-imprinted OCMC beads and 70.0 mL ethanol were mixed with the prepared thiourea/glutaraldehyde solution and heated to 70 °C, shaking at 150 rpm for 8 h. The ITG-OCMC beads were then filtered and washed with dilute sodium hydroxide, deionized water, and finally acetone. The beads were air dried for 48 h to remove the acetone then stored in deionized water.

4.2.2.4 Desorption of ITG-OCMC beads

Water solution containing 3.500 wt% of thiourea and 0.07500 vol% of H_2SO_4 was used to remove the template Ag^+ from the prepared ITG-OCMC beads. The mixture was under constant shaking at 150 rpm for 24 h. After desorption, the regenerated ITG-OCMC beads were filtered and rinsed with deionized water, then air-dried for 24 h and finally stored in sealed bottles until use.

4.2.3. Adsorption Experiments

To study the pH effect on the selective sorption of Ag^+ by the prepared ITG-OCMC beads, 100.0 mL bimetallic solutions containing 1.000 mmol L^{-1} $AgNO_3$ and 1.000 mmol L^{-1} $Cu(NO_3)_2$ with different pH values were prepared and mixed with 100.00 mg ITG-OCMC sorbent under constant shaking at 150 rpm for 24 h at room temperature. After filtration, the filtrates were analyzed by ICP-OES to determine the residual concentrations of metal ions in the solutions. The amount of adsorption, q_i (mg g^{-1}) for of each metal ion (i= Ag^+ or Cu^{2+}) can be calculated by Eq. (4-1).

$$q_i = \frac{(c_{i,0} - c_{i,e})V}{W} \qquad \text{Eq. (4-1)}$$

where $c_{i,0}$ and $c_{i,e}$ (mg L^{-1}) are the initial and final concentrations of metal ions in

the solution; V (L) is the volume of bimetallic solution and W (g) is the weight of the dry biosorbent.

Experimental investigation on the sorption kinetics was carried out batchwise at 25 °C for 48 h. 100.0 mL bimetallic solutions with an initial concentration of 0.5, 1.000, 1.500 and 2.000 mmol L^{-1} for each metal ion were fully mixed with 100.00 mg ITG-OCMC sorbent and shaken at 150 rpm in the incubator. Samples of 5.0 mL solution were taken at scheduled time interval and filtered for later concentration measurement by ICP-OES.

Adsorption isotherms were studied at temperatures of 10, 25 and 40.0 °C respectively. The initial metal concentration varies from 0.2500 mmol L^{-1} to 2.000 mmol L^{-1} for each metal ion. The liquid and solid phases were assumed to reach equilibrium after 48 h of sorption experiments.

Metal-saturated ITG-OCMC beads were desorbed using dilute sulphuric water solution (0.07500 vol%) containing 3.500 wt% thiourea. The regenerated beads were used in the next cycle of adsorption experiments. In total 5-cycles of adsorption-desorption experiments were performed at room temperature.

4.2.4. Analytical methods

The pH value of sample solutions was measured by an Accumet pH meter, AB 15^{+} (Fisher Scientific, Canada). Perkin Elmer Optima 5300DV (Perkin Elmer, Canada) inductively coupled plasma optical emission spectrometer (ICP-OES) was used to determine the concentration of metal ions. The Fourier transform infrared (FTIR) spectra of ITG-OCMC beads before and after metal uptake were recorded by a Tensor 27 FTIR spectrometer (Bruker, Germany). All samples were prepared as KBr pellets

and scanned in the wavenumber range of 400-4000 cm^{-1} at room temperature. X-ray photoelectron spectra of ITG-OCMC beads were obtained on an AXIS 165 X-ray photoelectron spectrometer (Kratos Analytical, USA) with Al Kα X-ray source.

To ensure the accuracy and consistency of the experimental data, all experiments were strictly carried out following the methods mentioned above and instructions of all equipment, all data were collected at designed time point, and all samples were tested by trained technicians.

4.3. RESULTS AND DISCUSSION

4.3.1. Sorbent screening

Adsorptions of Ag^{+} and Cu^{2+} on biosorbents prepared under different conditions are summarized in Table 4.1. Sorbents prepared with Ag^{+}-imprinting (ITG-OCMC beads) have much higher uptake capacities than those without Ag^{+}-imprinting (TG-OCMC beads), while all the prepared biosorbents show superb selectivity towards Ag^{+} and the presence of Cu^{2+} in competitive adsorption environment did not seem to affect the uptake of Ag^{+}. Results from Table 4.1 also indicate that the degree of carboxymethylation substitution and the amount of crosslinking agent used for the synthesis of ITG-OCMC beads significantly affect the selective uptake capacity of Ag^{+}. The highest selective adsorption of Ag^{+} (79.65 mg g^{-1}) occurred when a molar ratio of amino group of chitosan to carboxymethylation agent to crosslinking agent of 6:15:16 (No.1 in Table 4.1) is used. Thus, the ITG-OCMC beads prepared under this condition have been chosen for further experiments.

Table 4.1. Adsorption of Ag^+ and Cu^{2+} on sorbents prepared under different conditions

No.	Mole ratio of amine : acid	Mole ratio of amine : crosslinking agent	Imprinted or Not	q_{Ag} mg g^{-1}	q_{Cu} mg g^{-1}
1	2:5	3:8	Y	79.65	0.37
2	2:5	3:8	N	43.91	0.49
3	2:5	3:16	Y	39.19	0.26
4	2:5	3:16	N	35.00	0.10
5	4:5	3:8	Y	44.59	0.50
6	4:5	3:8	N	32.53	1.25
7	4:5	3:16	Y	47.00	0.82
8	4:5	3:16	N	38.08	0.61

Note: Batch sorption tests were carried out at T=25.0 °C with solutions containing 1.000 mmol L^{-1} of $AgNO_3$ and 1.000 mmol L^{-1} $Cu(NO_3)_2$ initially (pH≈4.8), shaking at 150 rpm for 24 hours.

When comparing the sorbent performance, it is observed that Ag^+-imprinting helps to remarkably enhance the uptake capacity of Ag^+ regardless of the degree of carboxymethylation substitution and level of crosslinking. However, such improvement is more significant when higher degree of carboxymethylation and lower level of crosslinking were combined. In addition, higher degree of carboxymethylation favours the binding of Ag^+ if low level of crosslinking was applied. On the contrary, uptake capacity of Ag^+ slightly increases with lower degree of carboxymethylation when high level of crosslinking was applied. This might due to the introduction of new binding sites provided by Schiff base.

4.3.2. Characterization of ITG-OCMC beads

Fig. 4.1 shows the IR spectra of chitosan powder, the prepared TG- and ITG-OCMC beads. The characteristic peaks of chitosan powder are: 3449 cm^{-1} corresponding to –NH and –OH stretching vibration; 1654 cm^{-1} due to –NH deformation vibration; 1154 cm^{-1} for –CN stretching vibration and 1079 cm^{-1} due to stretching vibration of –C-OH. Structure changes of TG- and ITG-OCMC beads were confirmed from their IR spectra. The –NH and –OH stretching vibration peak was completely shifted to two peaks at 3567 cm^{-1} and 3147cm^{-1} in the spectrum of TG-OCMC as the results of amino and hydroxyl groups of chitosan being substituted. Peak at 1079 cm^{-1} was shifted to 1060 cm^{-1} for TG-OCMC and 1103 cm^{-1} for ITG-OCMC. Together with the disappearance of the peak around 1154cm^{-1}, the carboxymethylation reaction could be confirmed to have taken placed on –C-OH (Wang et al., 2010). The new bands near 1629 cm^{-1} and 1544 cm^{-1} are assigned to stretching vibrations of C=N of Schiff base moiety and C-N of thiourea moiety (Donia et al., 2008), indicating the successful crosslinking of O-CMC with a polymeric Schiff base of thiourea/glutaraldehyde on the –C-NH_2.

Compared with TG-OCMC, the peak shift at 3449 cm^{-1} was minor for ITG-OCMC beads, which implies more amino and hydroxyl groups are remained due to Ag^{+}-imprinting. Because of the incomplete removal of template Ag^{+} during sorbent preparation, a new band at 618 cm^{-1}, which is assigned to stretching frequencies of metal-N bonds, suggests the formation of silver complex during the sorbent synthesis (Kuamr Naik et al., 2014).

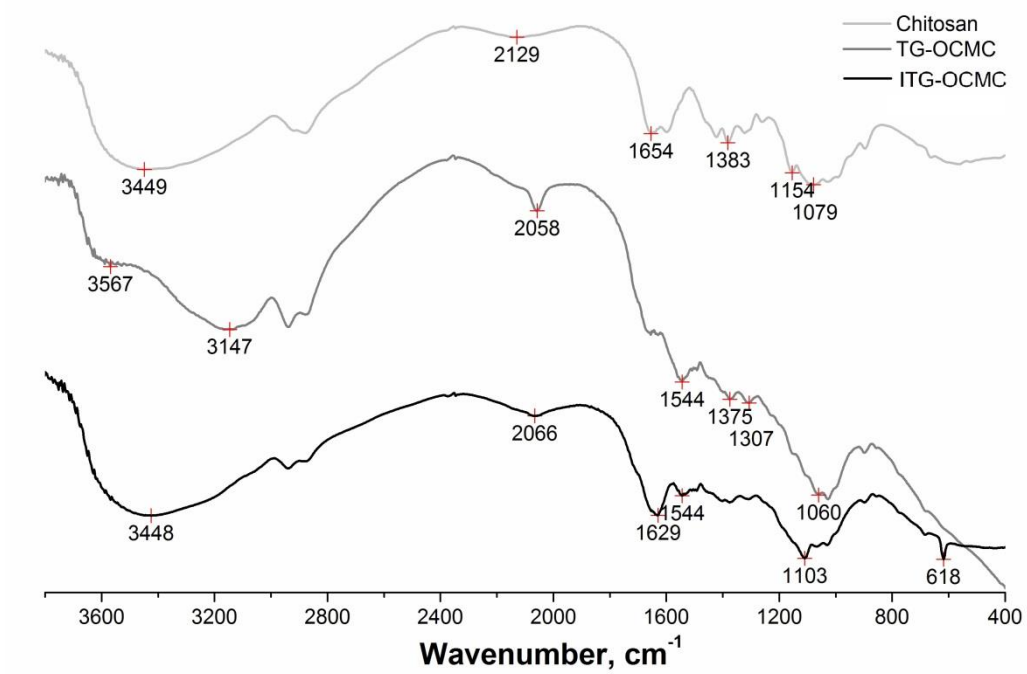


Figure 4.1. IR spectra of chitosan powder, TG- and ITG-OCMC beads

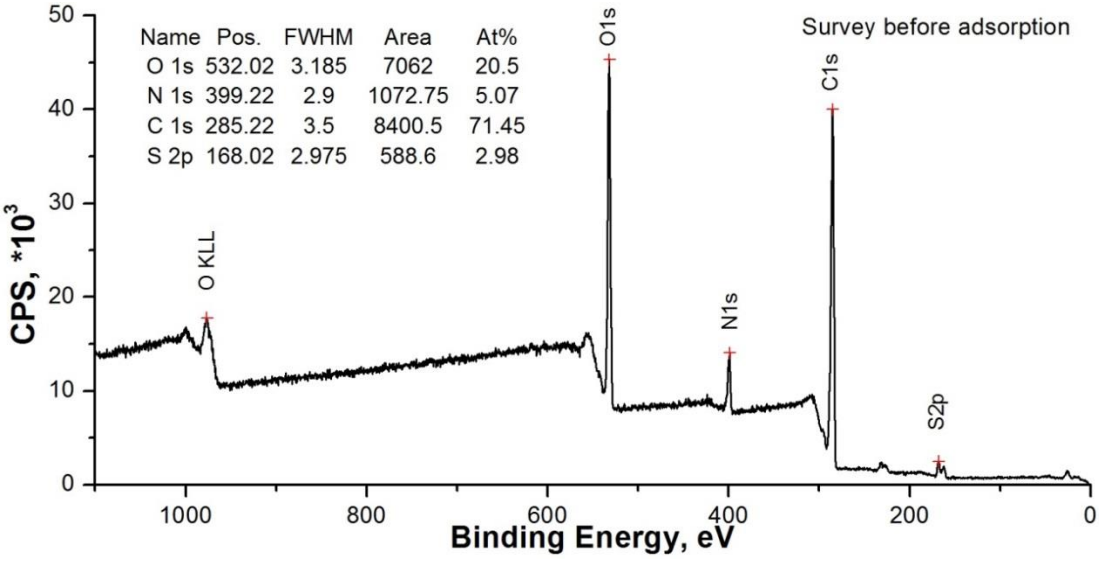


Figure 4.2. XPS survey spectrum of ITG-OCMC beads

XPS was also used to characterize the surfaces of ITG-OCMC beads. The XPS survey spectrum of ITG-OCMC beads (before metal uptake) is shown in Fig. 4.2. Coupled with the binding energy (BE) peak at 284.6 eV for C 1s, 533 eV for O 1s and 399.7 eV for N 1s as well as the S 2p peak with a BE around 166 eV are clearly visible, indicating the carboxymethylating agent and Schiff base agent were immobilized on the surface of chitosan.

4.3.3. Selective sorption mechanism of Ag^+

Results from Table 4.1 indicate that thiourea/glutaraldehyde grafted CMC beads with or without Ag^+-imprinting all show the extremely good selectivity towards Ag^+ over Cu^{2+}. It is therefore reasonable to conclude that biosorption of Ag^+ and Cu^{2+} take place at different sorption sites through different binding mechanisms. The amine group in chitosan is considered to be the most important feature in the adsorption of metal ions especially in transition metals (Rhazi et al., 2002; Guibal, 2004; Guibal et al., 2014). Several studies reported that Cu^{2+} is bound with amine groups of chitosan via inter- or intramolecular complexation (Schlick, 1986; Rhazi et al., 2002). According to Domard, chitosan forms a complex, with the structure close to $CuNH_2(OH)_2$ below pH 6.1 (Domard, 1987). However, carboxymethylating and thiourea/glutaraldehyde grafting of chitosan consume both –OH and $–NH_2$ groups, which reduces the available binding sites for Cu^{2+}. As a result, Cu^{2+} adsorption through surface complexation with ITG-OCMC or TG-OCMC beads was greatly hindered.

Selective uptake mechanism of Ag^+ over Cu^{2+} can also be found from the molecular structure of TG- and ITG-OCMC beads. As the Shiff base crosslinker has a relatively long carbon chain, the distance between different chains of OCMC is too long

to form chelations. Particularly, Cu^{2+} is more electropositive than Ag^{+}, more electron-donating atoms need to be involved to bind Cu^{2+} via chelation. However, Ag^{+} can easily bind to the surfaces of beads through chelation with free amino and hydroxyl groups.

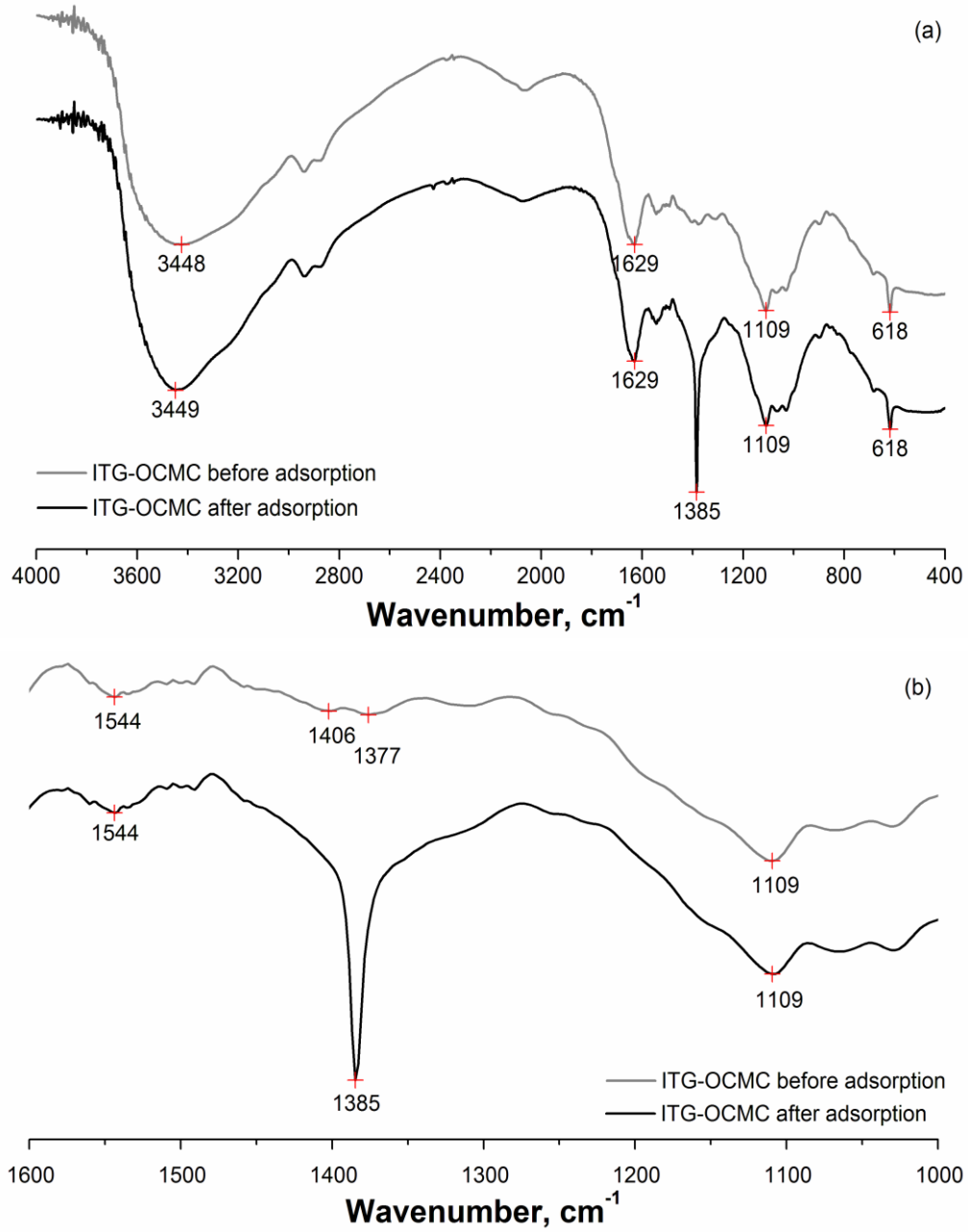


Figure 4.3. IR spectra (a) and expanded spectra (b) of ITG-OCMC beads before and after metal uptake.

The major functional groups involved in Ag^+ uptake were believed to be >C=S, $-NH_2$, –COOH and -OH groups on the sorbent surfaces. According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, >C=S group has a high affinity towards Ag^+ (Won et al., 2014). The IR band shift from 1377 cm^{-1} to 1385 cm^{-1} shown in Fig. 4.3 confirms that sulphur groups contribute significantly to the uptake of Ag^+ on sorbent surface. Carboxyl group on ITG-OCMC plays a very important role in selective uptake of Ag^+ in this case, which can be confirmed by comparing the sorption performances of beads No. 1-4 in Table 4.1. The improved uptake capacity at a higher degree of carboxymethylation of $–CH_2OH$ group proved the involvement of –COOH group in Ag^+ uptake. The evidence from IR spectra of ITG-OCMC beads (Fig. 4.3b) before and after Ag^+ and Cu^{2+} adsorption supports the involvement of carboxyl group in Ag^+ uptake. Bands at 1544 cm^{-1} and 1406 cm^{-1} on the IR spectrum of beads before sorption are due to the asymmetrical and symmetric C=O stretching of -COOH group (Choong and Wolfgang, 2003; Zhou et al., 2009). Band at 1385 cm^{-1} in the IR spectrum of ITG-OCMC after metal uptake is the combined effect of band shifts at 1406 cm^{-1} and 1377 cm^{-1}.

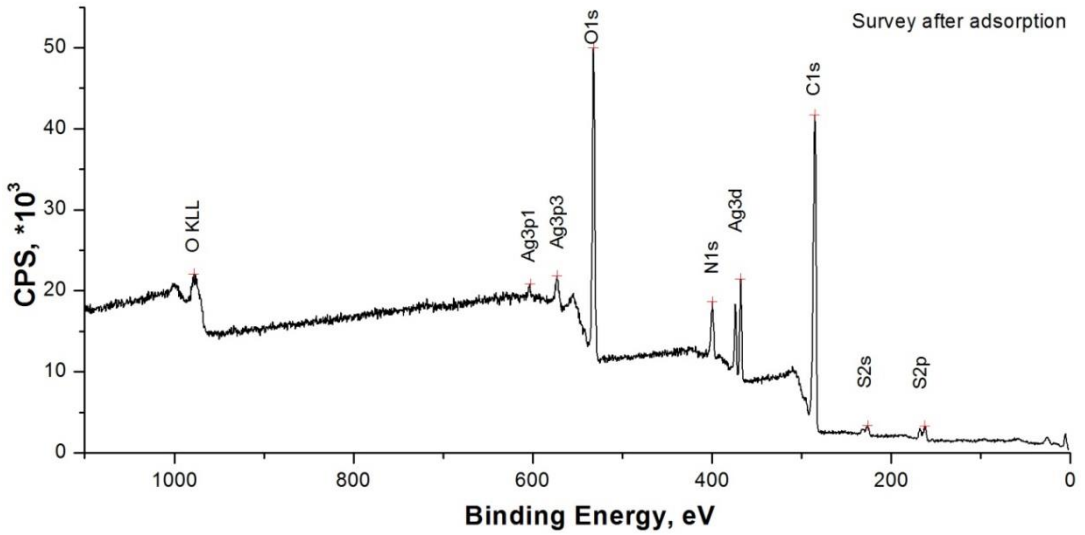


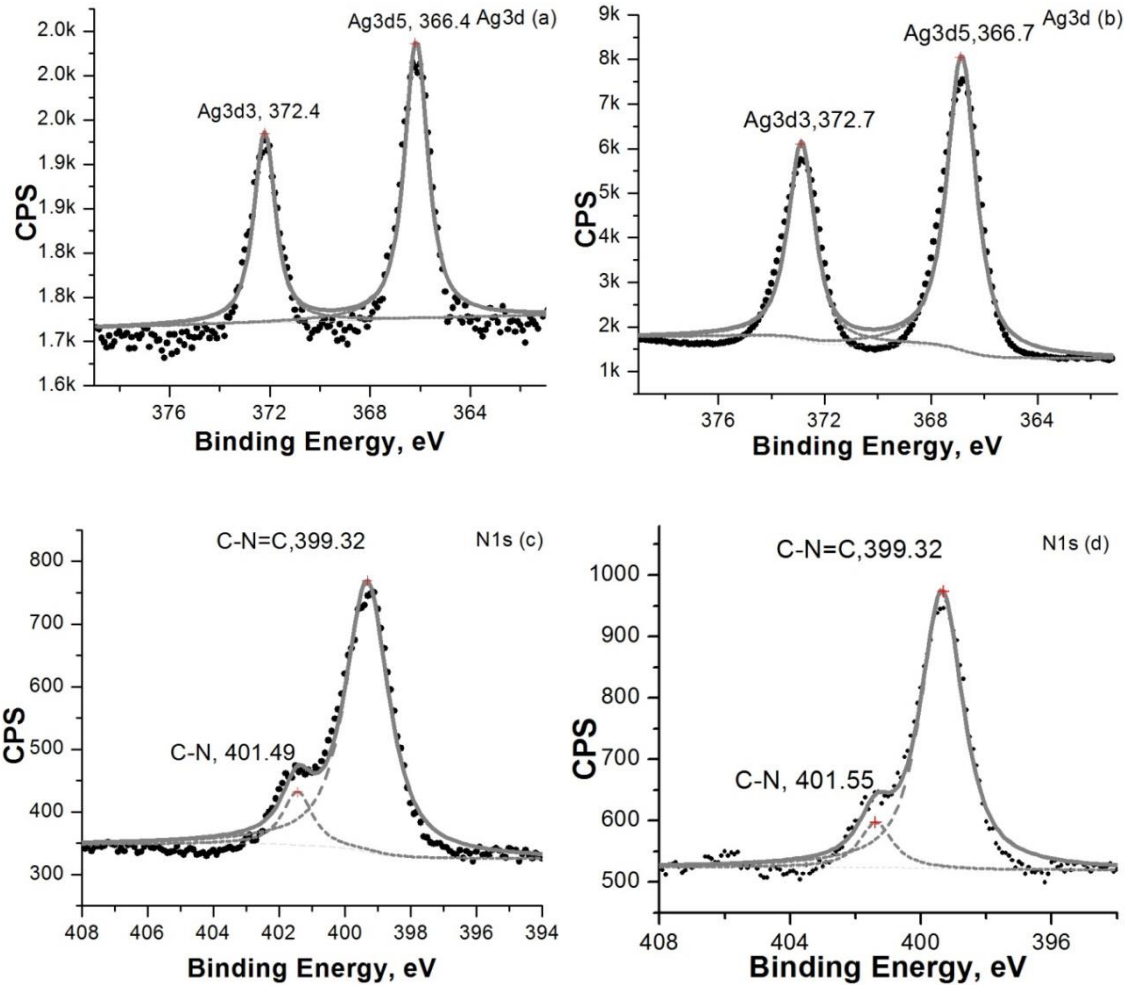
Figure 4.4. XPS survey spectrum of ITG-OCMC beads after metal sorption

To examine the selective adsorption mechanism, XPS analysis of the ITG-OCMC beads after metal uptake was conducted. The survey spectrum shown in Fig. 4.4 indicates the presence of carbon, oxygen, nitrogen, sulphur and silver. The photoemission bands Ag3d, Ag3p1, and Ag3p3 showed a significant amount of Ag^+ has been adsorbed. Further, based on the high resolution spectra, the doublet of Ag3d in Fig. 4.5a is assigned to compounds formed between S and Ag. The BE shift is only 0.1 eV after metal uptake (Fig. 4.5b) although the intensity of the peak increases significantly. This result suggests that a significant amount of Ag^+ is bound to the sites which are previously occupied by the template Ag^+.

High resolution XPS spectra of N 1s and S 2p of the sorbent before and after metal uptake are compared in Figs. 4.5c-4.5f. Two BE peaks at 399.3 and 401.5 eV are visible for N 1s spectrum before sorption. The N atom has two chemical states in ITG-OCMC beads before adsorption, which are C-NH_2 and C=N-C in the network. The N atom in C=N-C group has more negative charge than the one in the primary amine. As a result, the peaks at 399.3 and 401.5 were attributed to C=N-C and C-NH_2, respectively. After metal uptake, peak of C-NH_2 shifted to higher binding energy while peak of C=N-C at 401.5 eV remained the same. The band shift of N 1s spectrum after metal uptake indicates that the association of Ag^+ to primary amine group leads to a decrease of the electron cloud density of the nitrogen atom and the C=N-C group is not much involved in silver binding.

Four peaks are observed from the high resolution S 2p spectrum before metal sorption. Peak at 168.0 eV is assigned to the sulfur atoms in -SO_x (contaminated S). The unresolved peaks at 163.4 and 162.1 eV correspond to the sulfur bound to Ag^+

(Bootharaju and Pradeep, 2011). The peak at 161.1 eV is contributed to the sulfur in the >C=S group (XPS database chemical shift). The appearance of the peaks at 163.4 and 162.1 eV in the spectrum before sorption indicates that desorption of imprinted Ag^+ was incomplete. Significant band shift at 161.1 eV was observed from the spectrum of S 2p after sorption. The peak shift at 161.1 eV to higher BE leads to an increased intensity of the peak at 162.1 eV, which proves the involvement of >C=S group in Ag^+ binding. The O1s XPS spectrum of ITG-OCMC beads before and after metal sorption only shows a slight shift towards the higher BE, indicating that O atoms were also involved in Ag^+ adsorption. The electron density of O atom which acts as the electron donor, decreases during the sorption process.



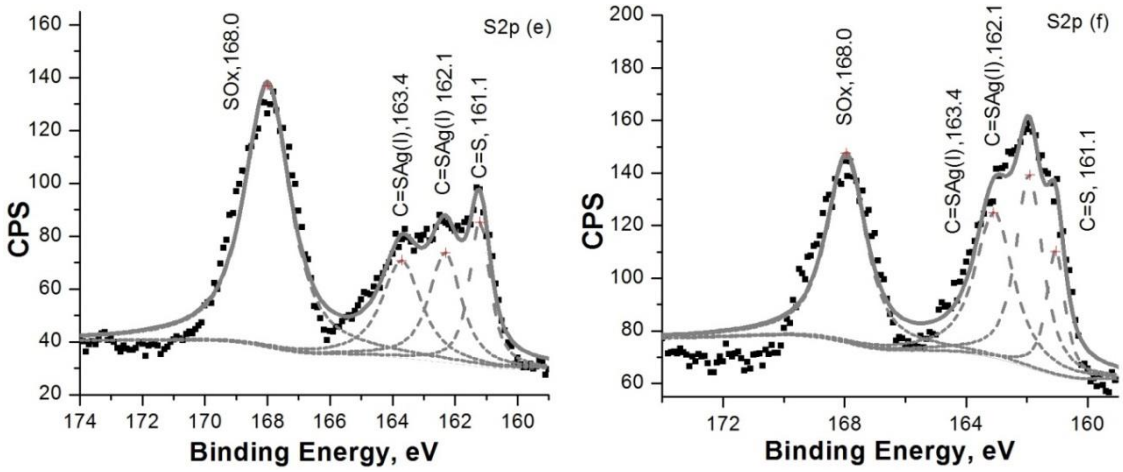


Figure 4.5. Fitted high-resolution photoemission spectra of Ag 3d, N1s and S 2p before (a), (c), (e) and after (b), (d), (f) metal uptake for ITG-OCMC beads. Label: (•) recorded signals; (—) Voigt-type fitted curves; and (- -) deconvoluted regions from the fitted curves.

4.3.4. Effect of pH

Results of Ag^{+} and Cu^{2+} uptake by the ITG-OCMC beads at different initial pH are shown in Fig. 4.6. The uptake capacity of metal ions increases as the initial pH of the bimetallic solution increases from 1.0 to 6.0. Reduced uptake capacity of ITG-OCMC beads at lower pH may be due to the protonation of the amino groups in low pH environment, which results in the reduction of number of binding sites available for the adsorption of both Ag^{+} and Cu^{2+}. The differences of uptake capacity of the ITG-OCMC beads at pH 4.0, 5.0 and 6.0 are less than 4%, which can be considered as insignificant variations. As the pH of the bimetallic solution containing 1.000 mmol L^{-1} $AgNO_3$ and 1.000 mmol L^{-1} $Cu(NO_3)_2$ is around 5.0, further sorption tests were conducted without adjusting the pH of the bimetallic solution. Abolishing pH adjustment means less chemical were consumed during the sorption test, which is better both environmentally and economically.

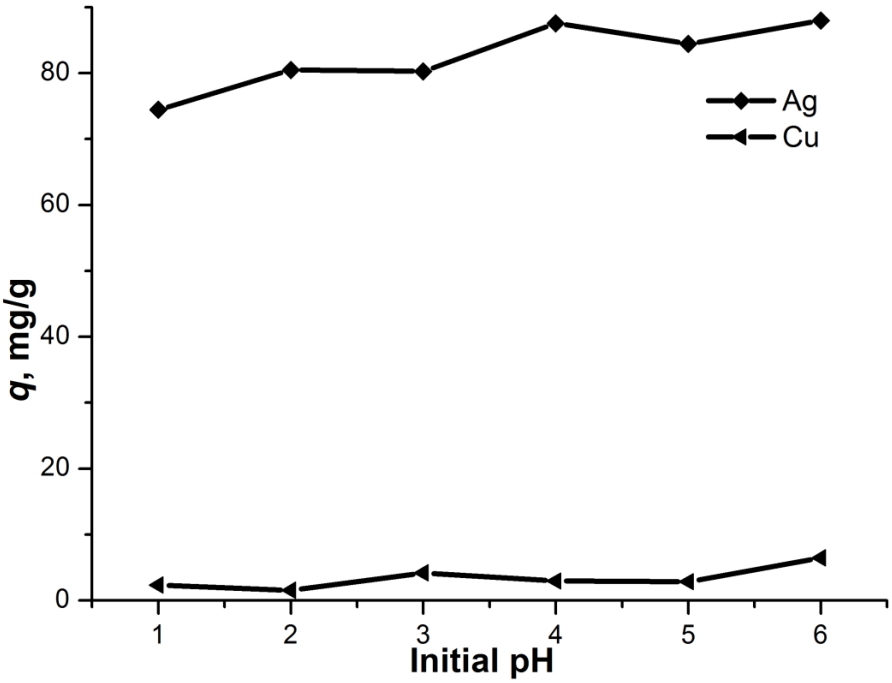


Figure 4.6. Effect of pH on the uptakes of Ag^{+} and Cu^{2+}

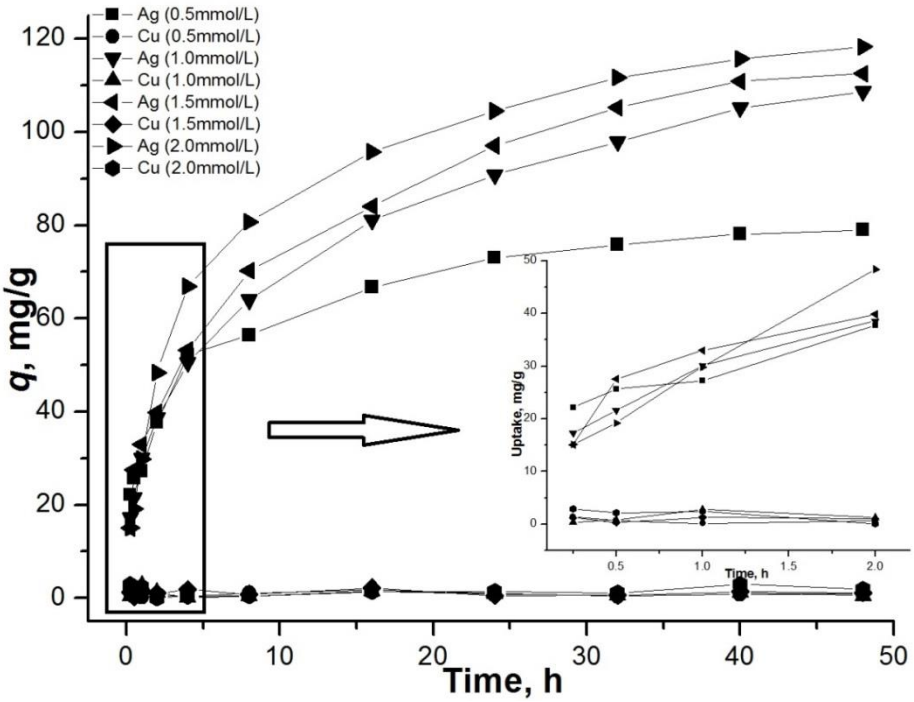


Figure 4.7. Effect of contact time on the uptakes of Ag^{+} and Cu^{2+}

4.3.5. Adsorption kinetics of Ag^+

The effect of contact time on the biosorption of Ag^+ and Cu^{2+} is demonstrated in Fig. 4.7. The kinetic curve shows that adsorption of Ag^+ was rapid for the first 4 hours. After that the sorption of Ag^+ became slower. Due to the low mass transfer rate of Ag^+ in the pores of ITG-OCMC beads, adsorption equilibrium was almost reached after 48 hours. No significant sorption of Cu^{2+} was observed during this study.

In order to evaluate the kinetic mechanism that controls the biosorption process, pseudo-first-order (Largergren, 1898) and pseudo-second-order (Ho, 2006) equations were employed to interpret the experimental data. As Cu^{2+} is scarcely adsorbed by the ITG-OCMC beads, kinetic rate constants for the Cu^{2+} uptake were not incorporated in this study. The pseudo-first-order equation is in the form of,

$$q_t = q_e(1 - \exp^{-k_1 t}) \qquad \text{Eq. (4-2)}$$

where k_1 (h^{-1}) is the pseudo-first-order biosorption rate constant, q_t (mg g^{-1}) is the amount adsorbed at time t (h), and q_e (mg g^{-1}) is the amount adsorbed at equilibrium.

The pseudo-second-order equation can be expressed by,

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad \text{Eq. (4-3)}$$

The linear form of pseudo-second-order equation is as below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad \text{Eq. (4-4)}$$

where k_2 (g mg^{-1} h^{-1}) is the pseudo-second-order biosorption rate constant, while all the other parameters have the same physical meanings as those in the first order

equation. The initial adsorption rate, h (mg g^{-1} h^{-1}), can also be calculated by Eq. (4-5).

$$h = k_2 q_e^2 \qquad \text{Eq. (4-5)}$$

The kinetic parameters for the rate equations were determined by nonlinear curve fitting using Origin8.6 software for pseudo-first-order, and the linear curve fitting for pseudo-second-order. The results are shown in Table 4.2. Pseudo-second order model gave better correlations than the first-order model for the sorption rate of Ag^+ from different initial concentration as illustrated in Fig. 4.8.

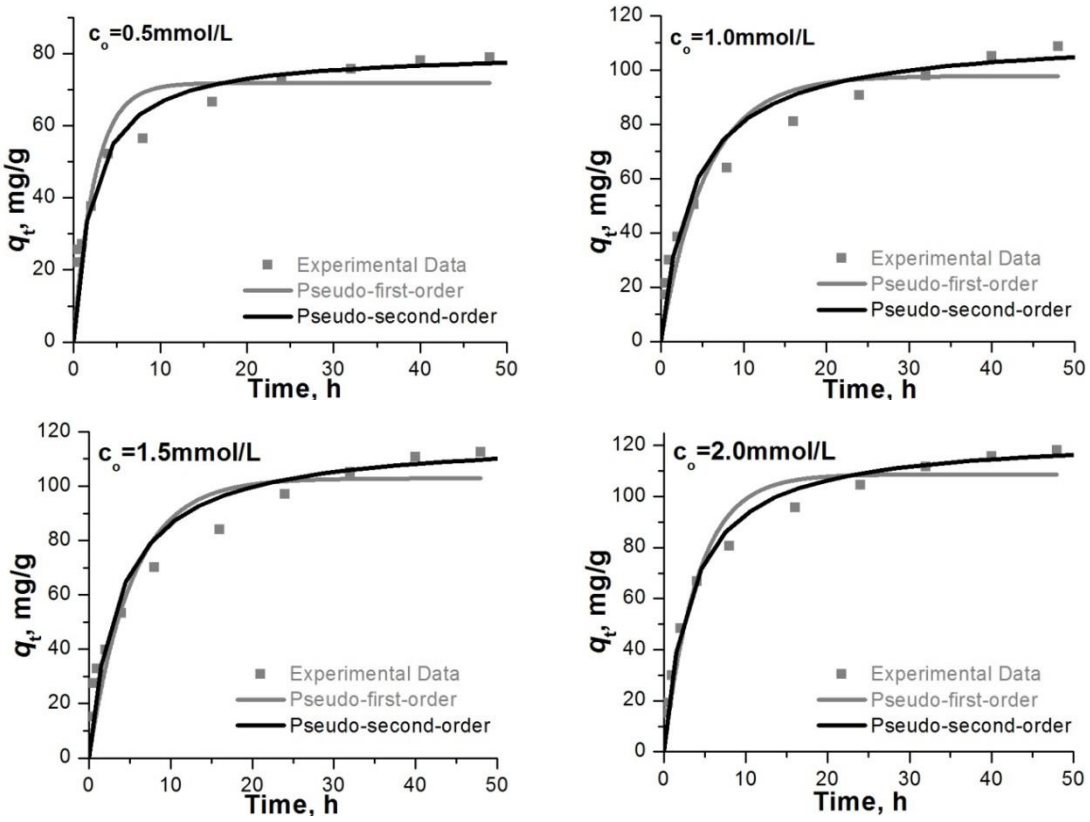


Figure 4.8. Adsorption kinetics of Ag^+ at 25.0 °C with different initial concentrations

Table 4.2. Kinetic parameters of the adsorption of Ag^+ on ITG-OCMC beads

Initial Concentration mmol L^{-1}	**Pseudo-first-order**			**Pseudo-second-order**			
	k_1 h^{-1}	q_e, mg g^{-1}	R^2	k_2 g mg^{-1} h^{-1}	q_e, mg g^{-1}	h mg g^{-1} h^{-1}	R^2
0.5	0.409	71.871	0.840	5.820×10^{-3}	80.775	37.994	0.997
1.0	0.183	97.816	0.900	2.260×10^{-3}	112.994	28.818	0.989
1.5	0.192	102.869	0.897	2.270×10^{-3}	118.203	31.676	0.991
2.0	0.242	108.681	0.955	2.430×10^{-3}	124.069	37.411	0.997

4.3.6. Adsorption isotherm of Ag^+

The effect of temperature on the adsorption equilibrium of Ag^+ on the ITG-OCMC biosorbent was demonstrated in Fig 4.9a. It is observed that equilibrium uptake capacity of Ag^+ increases when the temperature is raised from 10.0 to 40.0 °C. This result indicated that the binding of Ag^+ on ITG-OCMC is endothermic.

Both Langmuir and Freundlich isotherm models (Ruthven, 1984) were used to describe the amount of Ag^+ adsorbed and its equilibrium concentration in aqueous solution. The Langmuir and Freundlich equations are given in Eqs.(4-6) and (4-7), respectively,

$$q_e = \frac{q_s b c_e}{1 + b c_e} \qquad \text{Eq. (4-6)}$$

$$q_e = K_F c_e^{1/n} \qquad \text{Eq. (4-7)}$$

where q_e (mg g^{-1}) is the amount of Ag^+ adsorbed at equilibrium, c_e (mg L^{-1}) is the equilibrium concentration of Ag^+ in solution, q_s (mg g^{-1}) is the maximum biosorption capacity, b is the sorption equilibrium constant, K_F is a constant indicative of the

adsorption capacity of the sorbent, and $1/n$ is a measure of adsorption intensity.

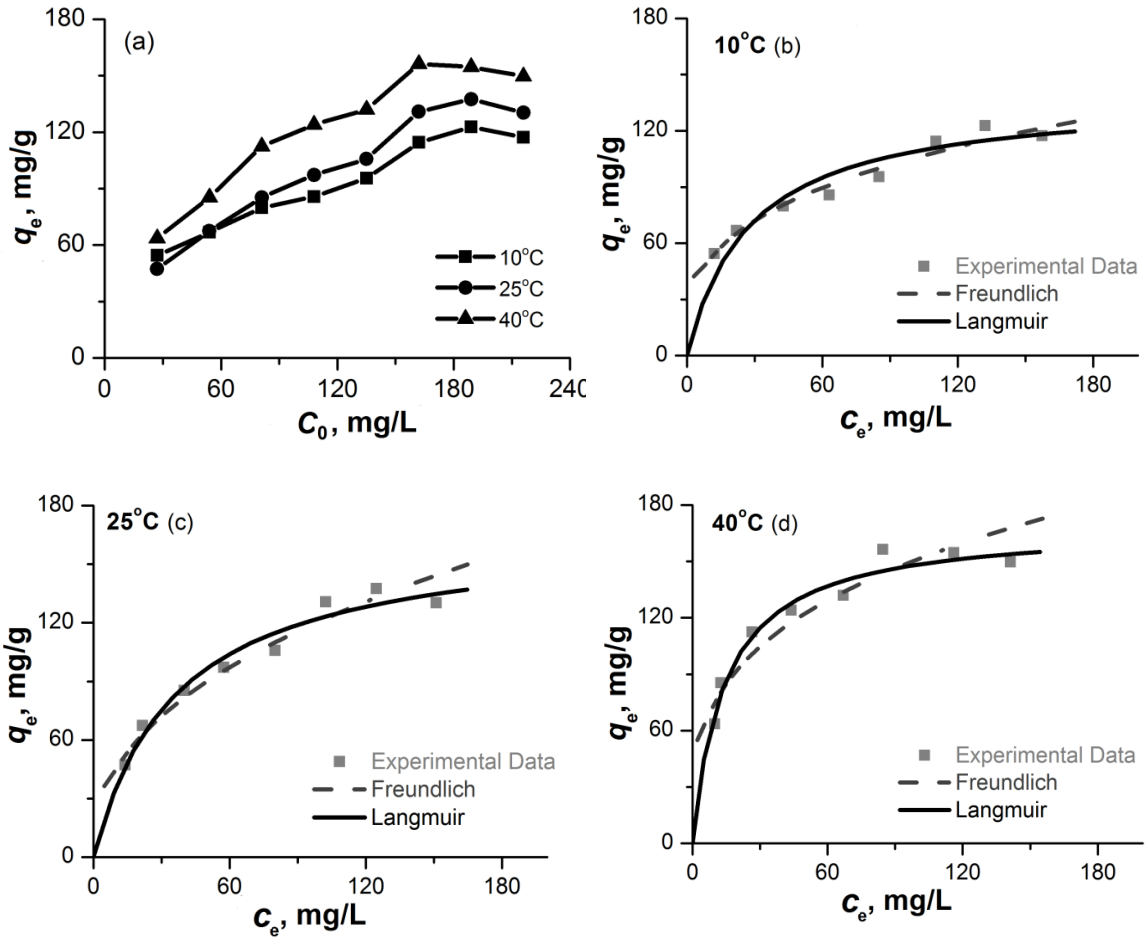


Figure 4.9. Adsorption isotherm of Ag^+ at different temperatures

Langmuir and Freundlich models can be converted into linear forms as shown in Eqs. (4-8) and (4-9) and the isotherm parameters can be determined by linear regression. The determined Langmuir and Freundlich isotherm parameters can be found in Table 4.3.

$$\frac{c_e}{q_e} = \frac{c_e}{q_s} + \frac{1}{q_s b} \qquad \text{Eq. (4-8)}$$

$$\log q_e = \log K_F + 1/n \log c_e \qquad \text{Eq. (4-9)}$$

Table 4.3. Isotherm parameters of the adsorption of Ag^+ on ITG-OCMC beads

T	**Langmuir**			**Freundlich**		
K	b L mg^{-1}	q_s mg g^{-1}	R^2	K_F	n	R^2
283.15	0.036	138.899	0.976	24.662	3.174	0.974
298.15	0.027	167.504	0.980	16.766	2.330	0.964
313.15	0.070	169.205	0.993	68.729	4.837	0.837

Results from Figs. 4.9b-4.9d indicate that Langmuir model represents the experimental data better than Freundlich model, especially at high temperature. Both Langmuir and Freundlich isotherms are favourable type of isotherm, indicating that ITG-OCMC is very effective in retaining Ag^+ from dilute solutions.

The enthalpy, ΔH (kJ mol^{-1}) and entropy, ΔS (kJ mol^{-1} K^{-1}) change of Ag^+ adsorption can be derived from the equilibrium constant b in Langmuir isotherm model based on the Van't Hoff equation listed below:

$$\ln b = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad \text{Eq. (4-10)}$$

where R is the universal gas constant and T is the absolute temperature (K).

The slope and intercept from linear plot of ln$b$ versus 1/T gave the values of $-\Delta H/R$ and $\Delta S/R$ respectively. Gibbs free energy change, ΔG (kJ mol^{-1}) was calculated by Eq. (4-11).

$$\Delta G = \Delta H - T\Delta S \qquad \text{Eq. (4-11)}$$

Thermodynamic parameters calculated from Eqs. (4-10) and (4-11) were listed in Table 4.4. The negative ΔG indicates that Ag^+ adsorption by the prepared sorbent is

spontaneous and thermodynamically favourable. The positive ΔH proves that the adsorption is endothermic in nature. The positive value of ΔS means the entropy increases during the adsorption, which has two possible reasons. First, according to Ringot et al. (2005) and Zhao et al. (2008), the positive value of ΔS may due to the decomposition of the hydration shell surrounding Ag^+, as Ag^+ usually presents in the form of $[Ag(H_2O)_4]^+$. Second, according to Gupta and Rastogi (2008), the increased entropy may also indicate that the randomness at the interface of sorbents and Ag^+ increases duo to the adsorbed Ag^+ on the surface of the sorbents. The results also indicate that $|T\Delta S| > |\Delta H|$, which means the adsorption of Ag^+ is dominated by entropic changes rather than the enthalpic changes.

Table 4.4. Thermodynamic parameters of the adsorption of Ag^+ on ITG-OCMC beads

T K	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS J mol^{-1} K^{-1}	$T\Delta S$ kJ mol^{-1}
283.15	-19.46			35.848
298.15	-19.81	16.922	126.67	37.748
313.15	-23.26			39.648

4.3.7. Sorbent reusability

The reusability of ITG-OCMC beads for the uptakes of Ag^+ and Cu^{2+} was illustrated in Fig. 4.10. It was revealed that the uptake capacity of Ag^+ almost remained the same after 5 desorption-biosorption cycles, and the Cu^{2+} was scarcely adsorbed in all five experiments. The results indicated that the prepared sorbent has good durability and high efficiency for repeated use. Obviously, more adsorption-desorption cycles

should be employed to provide a thorough evaluation on the sorbent reusability performance. However, batch mode adsorption-desorption is very time consuming, column adsorption test is a better choice for this purpose.

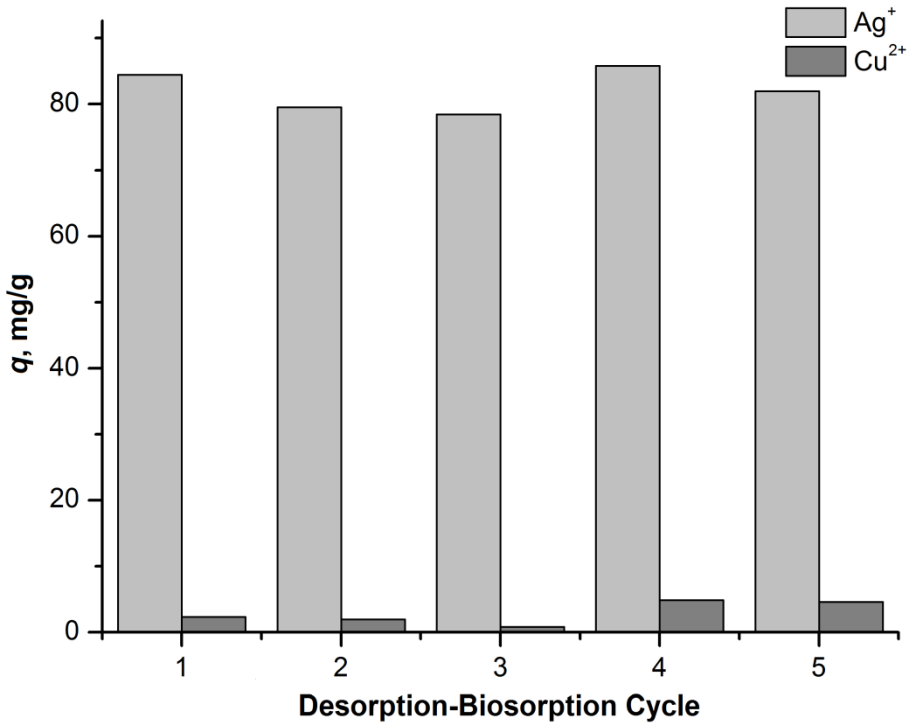


Figure 4.10. Reusability of ITG-OCMC beads

4.4. CONCLUSIONS

The selective biosorption of Ag^{+} from equal molar Ag^{+} and Cu^{2+} solutions was investigated using a novel synthesized ITG-OCMC sorbent. Results indicated that ITG-OCMC sorbent shows superb selectivity towards Ag^{+} in all ranges of initial concentrations and pH values. The maximum uptake of Ag^{+} is 156.32 mg g^{-1}sorbent at 40.0 °C. Langmuir isotherm and Lagergren's Pseudo-second-order rate equation can describe the sorption process very well. The reusability of the sorbent was proved to be

extremely good. Further analyses from FTIR and XPS confirmed that functional groups of >C=S, amine, carboxyl and hydroxyl involve the binding of Ag^{+} via chelation. The adsorptions of Ag^{+} with extended metal ions, such as Hg^{+}, Ni^{2+} and Zn^{2+} will be carried out in the next stage of study for a more broad-spectrum applicability of the ITG-OCMC sorbent.

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Chapter 5 Conclusions and Future Work

5.1. SUMMARY OF THE STUDY

In this study, two different approaches have been applied to prepare chitosan-based biosorbents with promising performance: one is to obtain an applicable chitosan-based sorbent with only immobilizing, imprinting and crosslinking procedures; the other is to prepare a chitosan based sorbent using crosslinking, imprinting, and grafting techniques or methods to enhance its capacity and selectivity. By applying the design of experiment (DOE) method and statistical analysis, optimal sorbent preparation processes were determined for subsequent experiments. Sorption performance was investigated and found to be satisfactory. Kinetic and isotherm studies were carried out on the prepared sorbents under different conditions, and the collected data was simulated by different kinetic and isotherm mathematic models. Dominant biosorption mechanisms were revealed based on the results of FTIR and XPS analyses.

5.2. RESEARCH ACHIEVEMENT

The selective biosorption of Ag^+ from equal molar Ag^+ and Cu^{2+} solutions was investigated using Ag^+-imprinted glutaraldehyde crosslinked chitosan (IGCC) and Ag^+-imprinted thiourea-glutaraldehyde-crosslinked O-carboxymethyl chitosan

(ITG-OCMC) beads. Experimental results indicated that both sorbents gave superb selectivity towards Ag^+ in all ranges of initial concentrations and pH values. The maximum uptake of Ag^+ is 156.32 mg g^{-1} sorbent at 40.0 ℃ for ITG-OCMC beads and 89.200 mg g^{-1} sorbent at 25.0 °C for IGCC beads. Compared with the results listed in Section 2.3, the prepared chitosan based beads show relatively high capacity and good selectivity. Langmuir isotherm and Lagergren's pseudo-second-order rate equations can describe the sorption process of ITG-OCMC beads very well, while Langmuir isotherm equation and intra-particle diffusion models provide good description of the sorption process of Ag^+ on IGCC beads. Further analyses of FTIR and XPS were used to confirm the functional groups involved in binding, and then deduce possible biosorption mechanisms. For the ITG-OCMC beads, >C=S, amine, carboxyl and hydroxyl groups were involved in the binding of Ag^+ via chelation; for the IGCC beads, amine functional groups were involved in the binding of Ag^+ via complexation at higher solution pH ($3.0 \leq pH \leq 5.0$) and ion exchange at lower solution pH ($1.0 \leq pH < 3.0$). The reusability of the ITG-OCMC beads was also investigated, and proved to be very good.

In summary, one of the achievements of current study is the preparation of two different kinds of chitosan-based biosorbents with relatively high capacity and good selectivity in bimetallic solutions, the other main achievement is that possible mechanisms of the selective sorption process were obtained based on the kinetic, thermodynamic and isotherm simulations and the analyses of XPS and FTIR results.

5.3. LIMITATIONS OF CURRENT WORK AND CORRESPONDING RECOMMENDATIONS FOR FUTURE WORK

In this study, all sorption tests were executed in bimetallic solutions with Ag^{+} and Cu^{2+}, so the adsorptions of Ag^{+} in competition with other metal ions, such as Hg^{2+}, Ni^{2+} and Zn^{2+}, should be carried out in the future to verify the broad-spectrum applicability of the sorbents because industrial wastewater and effluents contain various metal ions. The performance of sorbents in multi-metallic solutions is critical for industrial applications. Moreover, only batch experiments have been conducted in this study, while continuous column tests are probably a better predictor for the industrial applications of a sorbent. In future research, column tests should be carried out with various kinds of solutions. Furthermore, deionized water was used to prepare all solutions and wash beads and glassware to eliminate contaminants. However, for industrial applications, it is impossible to remove all unwanted components before column biosorption. As a result, the evaluation of sorbent performance should be carried out in solutions prepared with natural water.

From the sorbent preparation perspective, two aspects may possibly be improved in future research. First, only one desorption reagent was used for the removal of uptake metal ions from the sorbents, and the combination of thiourea and H_2SO_4 is quite harsh, which may not be suitable for the column test. Even though the desorption reagent has been proven to be effective, a simpler milder reagent should be

found. In addition, the size and shape of sorbent beads were not uniform, which may lead to channelling while being applied to column tests.

From the sorbent performance perspective, there is one critical disadvantage that has to be improved: the adsorption rate. As shown in Chapters 3-4, the adsorption of Ag^{+} using IGCC or ITG-OCMC beads needs more than 48 h to reach the equilibrium, the time is too long for these beads to be applicable in industries. The most possible reason for this is the structure of these beads. In order to accelerate the adsorption, more pores need to be generated on the beads, so the beads can have larger surface area. As a result, for future work, adsorbents need to be synthesized with larger surface area and better pore distribution.

In summary, for future work, sorbent performance with multi-matellic solutions prepared with natural water in a continuous column setup, as well as the evaluation of different desorption reagents, need to be implemented. From the sorbent preparation angle alone, a much milder reagent needs to be found, and equipment and operational methods need to be improved to acquire sorbent beads with more uniform shape and size.